Volume XXIV. *April, 1907.* *Number 4*

THE

PHYSICAL REVIEW.

ON THE MAGNETIC BEHAVIOR OF CERTAIN NICKEL ALLOYS.

By Bruce V. Hill.

THE work described in this paper was begun by the author several years ago at the University of Berlin and an abstract of the part then completed was published in the *Verhandlungen der Deutschen Physikalischen Gesellschaft.* It was not possible for me to obtain the material to finish the experiments till a few months ago. Meanwhile accounts of work by other experimenters upon kindred alloys have appeared, so that I have now collected their data together with my own.

There are two classes of alloys of the ferro-magnetic metals which are of particular importance: the steels and the alloys used in the construction of resistances. On the importance of the steels, it is unnecessary to comment. It is only recently, however, that it has been realized that the properties which render steel so universally useful are very closely connected with its magnetic characteristics. A few years ago the hardening of steel by sudden cooling was explained by supposing that, in the rapid fall of temperature, strains were set up in the metal which caused its hardness, or the hardness was accounted for by the presence of small particles of very hard carbon or of carbide. While this latter explanation may have been in part true, it is not sufficient to account for the phenomena of the tempering of steel. The electrolytic iron, which has been produced so successfully in the laboratories of the University of Wisconsin, is very hard when deposited. Dr. Taylor

informs me that it behaves like hard steel magnetically also, but after annealing it is soft, both mechanically and magnetically, like Norway iron. Certainly neither sudden cooling nor temper-carbon plays any part in this case. In making malleable castings of iron the annealing process changes the glass-hard, brittle cementite Fe_3C, into ferrite, or free iron, which is soft and ductile, mixed with finely divided carbon. The hard, brittle nature of the original casting seems to have been due, not to free carbon, but to a definite carbide, Fe_3C. As to the theory of hardness caused by internal strains, it is difficult to see why other metals than iron should not be hardened in the same manner.

The ordinary carbon-steel, having been once tempered or hardened, may have this temper or hardness withdrawn by annealing from a red heat. With the alloy steels, on the other hand, the case is entirely different. When nickel and iron are alloyed together, the product acquires something of the toughness of the nickel while retaining the hardness and high elastic limit of the iron. An exhaustive study of these alloys has been made by M. L. Dumas.[1] Only a few of these need be mentioned here. The non-expansive alloy of Guillaume contains 34 per cent. of nickel and has a coefficient of linear expansion of .000001. Clock pendulums made of this material vary so little in length that a clock thus provided will run more accurately than other clocks with the ordinary compensating devices. This alloy might also be useful in making fine instruments such as transits and the like. It will take a good polish and resist corrosion as well as nickel. Screws for dividing engines might also be made of it to advantage.

The steels with from 40 to 50 per cent. of nickel have so nearly the same coefficient of expansion as glass that they may be employed when it is desired to seal a metal into glass. This material, called "platinite," had already begun to replace platinum in the manufacture of incandescent lamps in France several years ago. These alloys do not seem as yet to be much known in this country. However useful the nickel-iron alloys of high per cent. may be, the high price of the nickel prevents their very extensive employment. An alloy containing from 3 to 3.5 per cent. of nickel and about

[1] Aciers au nickel a hautes teneurs.

0.25 per cent. of carbon combines a very high degree of ductility with a great tensile strength, hardness and a very high elastic limit. Such a steel, with the addition of a little chromium is used for the armor plate of vessels.

A small amount of manganese in steel, up to five or six parts in a hundred, renders it very brittle, but an alloy containing 12 per cent. of manganese and 1.5 per cent. of carbon is very hard but yet ductile. It is unmagnetic. Mushet discovered that, by the addition of manganese and tungsten to tool steel, a cutting edge could be maintained upon the tool at a temperature much higher than with carbon-steel. This, of course, made it possible to work these tools at a considerably greater speed. These steels, known as the self-hardening or air-hardening steels were hardened by slow cooling from a cherry-red, that is from about 900°C. If heated to a temperature much above this the quality of the steel deteriorated very rapidly. With the addition of a small amount of chromium and a little tungsten or molybdenum it was found that this deterioration at high temperatures was confined to a very narrow range, from about 850° to 950° C., while above 950° to about 1,100° the efficiency is greatly increased. These last steels are known as the high-speed steels of Taylor and White. Their alloy contains:

Carbon from 0.75 to 1.25 per cent.
Chromium from 3.00 to 4.00 per cent.
Tungsten 8.50 per cent.

The exact composition of the steel varies according to whether the tool is to be used for cutting soft steel or gray cast-iron, or hard steel. By employing tools made of such steel, the rate of cutting can be increased to three or four times that possible with a carbon-steel tool, since with a high-speed tool it may be allowed to heat till it shows a faint tinge of red. A large increase in efficiency is thus gained by the use of these tools. These alloy-steels are unmagnetic, a very small amount of manganese being sufficient to render the iron unmagnetic.

The second important group of alloys of the magnetic metals is that of the alloys used for electric resistances. These are mostly nickel alloys, the greater part of them being unmagnetic. Their resistance is higher than that of the pure metals while the tempera-

ture coefficient is lower. Manganin, for example, containing 84 per cent. of copper, 12 of nickel and 4 of manganese, retains its resistance almost constant between 0° and 30° C.

Seeing that the alloy-steels are hardened by annealing, whereas in the carbon-steels the hardening was accomplished by sudden cooling, it is evident that neither the theory of strains within the metal nor of hard carbon within its mass can account for its hardness, and the explanation was sought elsewhere.

The magnetic metals, if heated to a certain critical temperature, become unmagnetic and exhibit a much higher specific heat and a higher electric resistance together with a much smaller temperature-coefficient. The chemical properties also show differences above and below the critical temperature.

Again, if iron containing carbon be cooled from a high temperature there will be a marked evolution of heat at about 850° C. and another at 760° C. indicating some transformation in the metal itself. Osmond based his allotropic theory of the magnetic metals upon these phenomena. The iron as it exists at ordinary temperatures and up to 760° C. the lowest temperature at which the evolution of heat occurred (the temperature of recalescence is below 760° but is due to the separation of the eutectic alloy of iron and carbon, that is, the alloy containing 0.85 per cent. of carbon) Osmond called *alpha iron*. In the next interval, namely between 760° and 850° C., he applied the name *beta iron*, and above 860° *gamma iron*.

In nickel and cobalt the phenomena of transformation are very similar to those in iron, except that in these metals there are but two allotropic forms, the *alpha* and the *beta*.

Let us now return to the steels and apply the allotropic theory to explain their behavior. Let us suppose the *alpha iron* to be soft and magnetic; the *beta iron* hard, tough, rather brittle and unmagnetic; and the *gamma iron* soft and unmagnetic. At ordinary temperatures common iron and steel contain a mixture of the *alpha* and *beta* modifications. If pure iron be heated to a high temperature and cooled either rapidly or slowly, the transformations take place as usual and the metal remains soft. If the proper amount of carbon be added — 0.25 to 1.50 per cent. — and the metal be

suddenly cooled from a temperature above the critical point, a large amount of the *beta* iron persists and hardens the specimen. This is, of course, an incomplete account of these phenomena since the carbides of iron, which must also undergo transformations, have not been considered.

If any substance, other than carbon, could be added to the iron and prevent its transformation, we should expect to be able to alter the properties of the alloy in a way depending not only upon the nature of the added substance, but also upon the amount of *beta* and *gamma* iron present at ordinary temperatures. Lownds and Richardson [1] found that if aluminium be alloyed with iron the temperature of transformation of the latter is depressed by an amount proportional to the mass of aluminium added. This holds more or less closely for other elements alloyed with the iron. Osmond and van t'Hoff have worked out the phase diagram for iron and carbon alloys.[2] One of the most important results of the new knowledge of the physical chemistry of steels is the greater certainty with which a certain grade of steel can be produced. A comparatively inexperienced workman is able to secure more uniform results than were formerly obtained by men of much longer practice. A phase diagram has been given by Messrs. Shepard and Upton for alloys of copper and tin.[3]

If now there were some law by which the action of any element in alloy with iron could be predicted it would be of great value in steel-making. The most ready analogy to the depression of the temperature of magnetic transformation of iron and nickel by other metals alloyed with them, is the lowering of the freezing point of a liquid by dissolved substances. The law of van t'Hoff applying to the latter case is:

$$\Delta t = \frac{.02\,T^2 m}{ML}.$$

Where T is the absolute temperature of freezing of the pure solvent, .02 the thermo-dynamic constant, L the latent heat of fusion of the solvent, M the molecular weight of the solute and Δt the depression

[1] Phil. Mag. (6), 1, p. 601, 1901.
[2] The Metallographist, 1898.
[3] Journal of Physical Chemistry, 1905.

of the freezing point caused by m grams of the solute in 100 grams of the solvent. The present work was undertaken to test the applicability of this formula to the case in hand. To do this we would have to put T equal to the absolute temperature of transformation of the pure metal (nickel or iron), L the latent heat of transformation, M the molecular weight of the added metal and Δt the depression of the point of transformation caused by m grams of this metal. The derivation of van t'Hoff's formula assumes that the pure solvent freezes out. In attempting to apply this equation now it must be remembered that neither metal separates from the other at the point of transformation. Microscopic examination shows this to be true. We might hope, however, that the formula would apply approximately or in a modified form.

Nickel was chosen for these experiments rather than iron because of its low temperature of transformation, which being below 400° C. was easily reached and measured. The relations existing in alloys of iron and nickel are known to be very complicated so that, in order to have the conditions as simple as possible, the nickel could not be alloyed with any other ferro-magnetic metal. Nickel and copper can be alloyed in all proportions and such alloys are easily obtained. They were furnished me by the firm of Basse and Selve, in the form of wire. As one sees from the equation, the depression of the transformation point of the nickel in the alloy should be proportional to the percentage of the second metal and inversely proportional to the molecular weight of the latter. It was desirable therefore to obtain alloys with other metals having molecular weights as different as possible from that of copper. This was difficult however. We tried to get alloys of lead or bismuth or aluminium from the same firm who had supplied those of nickel and copper, but after several months they said that they were unable to make them. The firm of Haereus in Hanau finally succeeded in supplying some rings of alloys of nickel and tin containing 5, 10 and 15 per cent. of tin respectively.

There were four specimens of the nickel-copper alloys available. They were in the form of wires 2 millimeters in diameter and contained 4, 8, 20 and 40 per cent. of copper. To determine the relation between induction and temperature a secondary coil of bare

copper wire was wound about a glass tube and over this tube a primary coil 45 centimeters long and over both of these a heating coil of nickeline wire, the whole being insulated with asbestos. The wire under examination, together with a standard mercury thermometer, was put into the glass tube and the apparatus packed about with asbestos as heat insulation. The induction was measured ballistically, the throw caused by reversing the primary current being observed in each case. The material in order to be fit for these experiments had to be free from temperature hysteresis, like that in the irreversible nickel-steels. Experiments showed that the point of transformation with rising temperature was the same as with falling temperature. The 20 per cent. alloy was then held for an hour at a temperature of 100° C., a temperature near that of transformation, without any change in the induction in a given field being observed. It appears, then, that when a given temperature is reached the corresponding magnetic condition establishes itself without appreciable lag.

As is known, the loss of susceptibility does not occur suddenly, but gradually, through a wide interval of temperature. As one

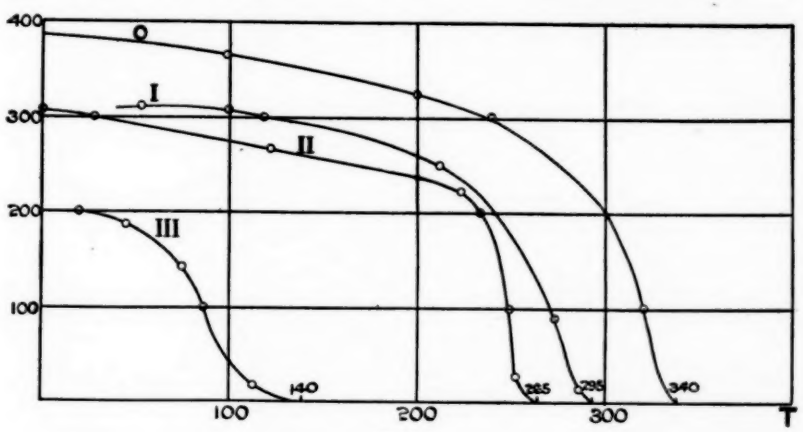


Fig. 1.

sees from the curves, taken from a field near that of saturation, the magnetic intensity, *I*, decreases with rising temperature very slowly at first and then more and more rapidly. When it has fallen to a small fraction of its original value, the decrease becomes much

slower. The temperature at which this occurs could be determined within 5°. The intensity-temperature curves for the pure nickel and the 4, 8 and 20 per cent. alloys are given in the figure. It will be seen that the analogy to the solidification of water does not hold for the transformation of the pure nickel. When water has reached the freezing point, the temperature remains constant till the solidification is complete, while the transformation of the *beta* into the *alpha* nickel is gradual. This can be explained if one assumes that the two phases are mutually soluble. As the microscope shows no difference between them, this assumption is permissible. We may suppose that as soon as a portion of the *beta* nickel has transformed into the *alpha* form it at once dissolves in the remaining *beta* metal and so lowers the transformation point requiring a

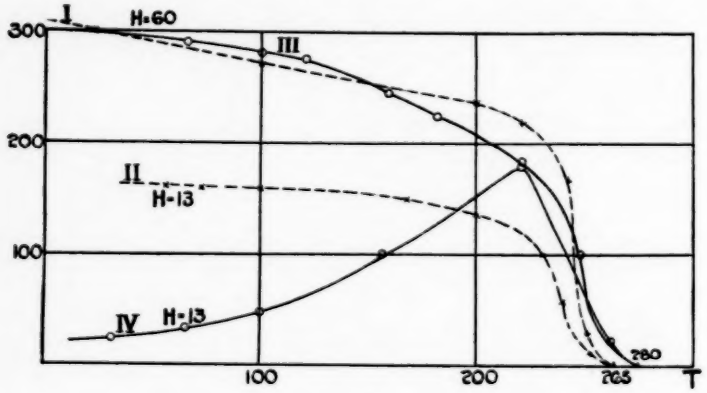


Fig. 2.

further fall of temperature before further transformation can occur. In the alloys this gradual fall of temperature with the progress of the transformation is to be expected as in the case of the freezing of a solution of salt in water.

The second figure gives the intensity-temperature curves for the 8 per cent. alloy in fields of 13 and 63 C.G.S. units respectively, The full line refers to the metal in the hard-drawn and the broken line to that in the annealed condition. The temperature of transformation appears to be independent of the field, but is lowered about 15° by annealing. This was true of the nickel and of all of the nickel-copper alloys.

The table shows the temperatures of transformation of the alloys of nickel and copper :

Per Cent. Cu.	Temp. (Hard).	Δt	Temp. (Annealed).	Δt	$\Delta t/m$
0	355°		340°		
4	310	45°	295	45°	11.2°
8	280	75	265	75	9.4
20	155	200	140	200	10.0
40	−100	455			11.4
					Mean 10.5°

According to this table the depression of the point of transformation is very nearly proportional to the amount of copper, m, in the alloy. Only in the first two alloys is the concentration small enough to justify the application of the formula of van t'Hoff, still the depression due to one part of copper in one hundred is so nearly constant that we may take the mean of these values.

Before the results just given could be applied in the formula, it was necessary to know the latent heat of transformation, L. This cannot be determined directly and at best can only be approximated by indirect methods. The values obtained in this way may give an idea of the order of magnitude of the quantity sought, however. The alloy containing 40 per cent. of copper, is unmagnetic at room temperature and so contains nickel in the *beta* condition. The specific heat of this alloy, as well as that of pure copper, was found between 20° and 370° C. That for the former was 0.1049 and for the latter 0.0996. If now we assume that the specific heat of this alloy can be found from those of its two constituents by the rule of mixtures, we have for the specific heat of the *beta* nickel

$$\frac{100 \cdot 0.1049 - 40 \cdot 0.0996}{60} = 0.1104.$$

A mass, m grams, of nickel was now heated to 370° and dropped into a water calorimeter whose water equivalent was K. The initial temperature was t_1 and the final temperature t_2. If the specific heat of the unmagnetic nickel just found is now introduced we have for the latent heat of transformation

$$L = C(370 - t_2) - K(t_2 - t_1)/m.$$

In five experiments the following values were obtained for L:

4.16
4.33
4.03
5.05
4.83
Mean 4.48

The agreement among these numbers is as good as the method would lead one to expect. In the first place the rule of mixtures holds only approximately for the specific heats of alloys. The specific heat was determined for the four nickel-copper alloys between 20° and 100°. If one takes 0.1100 for the value for nickel and 0.0933 for copper as found in the tables and calculates the specific heats of the alloys, he finds:

Alloy.	C (Observed).	C (Calculated).
4 per cent.	0.1080	0.1093
8	0.1141	0.1087
20	0.1145	0.1066
40	0.1003	0.1033

The agreement is not exact, and in the case of the 40 per cent. alloy the variation is 3 per cent.

By an entirely different method Pionchon[1] found the latent heat of transformation of nickel to be 4.64, a value not in bad agreement with that just given. Too much weight is not to be given to this agreement, however, as he found the latent heat of transformation as the difference between the quantities of heat given off when the metal was cooled first from a point just above and then from one just below the temperature of transformation, the latter point so high that the transformation was by no means complete. These values must at least give the order of magnitude of L however.

Before passing to the experiments upon other alloys of nickel and the further discussion of the formula it may be of interest to show the relation of the electric resistance of the nickel-copper alloys to their magnetic properties. H. Le Chatelier[2] and P. Harrison[3] have

[1] Ann. de chim. et de phys., 6, 11, p. 77, 1887.
[2] Compt. Rend., CX., p. 283, 1896.
[3] Phil. Mag. (6), 3, p 177, 1902.

given curves exhibiting the relation of the resistance to the temperature in nickel and iron. Fig. 3 gives similar curves for the 4, 8, and 20 per cent. alloys.

In all the specimens studied the temperature coefficient increases more or less rapidly till a temperature near to that of transformation

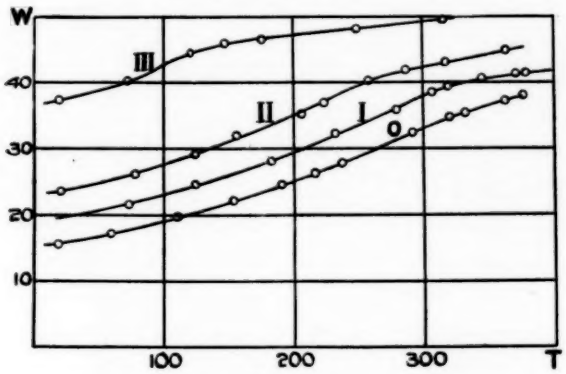


Fig. 3.

is reached. It then becomes smaller and nearly constant. This change is quite sharply marked though not so distinct as the magnetic transformation. It is plainer in the alloys than in the pure nickel. In the 20 per cent. alloy the change of direction of the curve is sharp and corresponds very closely to the transformation point.

I had three alloys of nickel and tin, containing 5, 10 and 15 per cent. of tin respectively. A microscopic examination showed them to be chemically homogeneous with no trace of free tin. Physically they were not uniform, however, as the metal was full of pores. The holes were the largest in the 5 per cent. and smallest in the 15 per cent. alloy. Alloys containing more than 20 per cent. of tin could not be cast and those with that amount were so porous that they could not be used. The specimens were in the form of rings. To determine the induction they were wound with insulated wire and heated in an oil bath, the temperature being measured with a mercury thermometer. With the ring containing 5 per cent. of tin the insulation gave way and it had to be rewound with bare wire and asbestos. The results for these alloys are given in the table :

Per Cent. of Tin.	Temp.	Δt	$\Delta t/m$
0	340°		
5	303	37°	7.4°
10	268	72	7.2
15	230	110	7.3
			Mean 7.3°

Here, as with the nickel-copper alloys, the depression of the transformation point is proportional to the amount of tin in the alloy. I will now compare the results found for the two series of alloys. The temperature of transformation for the pure nickel was 340° C. or 613° absolute. The latent heat of transformation of the nickel was 4.5 calories per gram. $\Delta t/m$ was equal to 10.5° for the copper and 7.3° for the tin. Introducing the above values for L and T into the equation of van t'Hoff, we have $\Delta t/m = 1670/M$. The molecular weight must therefore be known. If it were possible, the most direct way to determine the molecular weights of tin and copper in their solutions in nickel would be to apply the van t'Hoff formula to the lowering of the point of solidification of nickel by these metals dissolved in it. To do this, the latent heat of fusion of nickel would have to be known and this would be very difficult to determine as the melting point of nickel lies so high, in the neighborhood of 1600° C. Heycock and Neville [1] have made a series of experiments upon the lowering of the melting point of tin, thallium and sodium by alloying other metals with them. They found the "atomic lowering" of the metal point of tin by the solution of other metals in it, that is the depression caused by the alloying of one atomic weight of the given metal in 100 atomic weights of the tin, to have the following values.

For Nickel	2.94
Silver	2.93
Gold	2.93
Copper	2.91
Thallium	2.86
Sodium	2 84
Mean	2.90

If these metals in their alloys with tin are monatomic, the formula of

[1] Jour. Chem. Soc., 55, 666, 1889; Chem. News, 68, 305, 1893.

van t'Hoff gives, since $T = 504.5°$, $L = 14.25$ and the atomic weight of tin is 118.8 (later determinations give 118.5),

$$\Delta t = \frac{.02 \cdot T^2 m/118.8}{Lm} = .02 \cdot T^2/118.8 \cdot L = 3.01.$$

The agreement between this calculated value for the *atomic lowering* and the observed values seemed sufficiently close to warrant the conclusion that these metals are monatomic in their alloys with tin.

G. Meyer[1] found, from the electromotive force of cells whose electrodes were amalgams of different concentrations of the same metal, that the metals with which he experimented (Zn, Cd, Pb, Sn, Cu, Na) are monatomic in their solutions in mercury. The natural conclusion, then, seems to be that the metals have but one atom to the molecule. The probable correctness of this supposition will be discussed more fully later.

If then we assume that tin and copper are monatomic in their alloys with nickel and put the values of the atomic weights in the formula above given, we find (Cu = 63.6 and Sn = 118.5):

For	$\Delta t/m$ (Calculated).	$\Delta t/m$ (Observed).
Copper	26.3°	10.5°
Tin	14.1°	7.3°

The observed values are much smaller than the calculated. The lowering of the point of transformation is not inversely proportional to the atomic weight for, if this were the case, the depression caused by one per cent. of tin, as calculated from that observed to be due to one per cent. of copper would be 5.6° instead of 7.3°. The agreement would be better if we assumed two atoms to the molecule rather than one, but there is no reason for doing this. While the methods of Heycock and Neville and of Meyer show that the metals with which they experimented are monatomic at the melting point or when in solution in mercury, it is possible that in a solid condition the molecules may be highly associated. In fact the great departure from the law of Dulong and Petit at high temperatures might, perhaps, be accounted for in this way.

For other alloys of nickel the depression of the point of trans-

[1] Zeitschr. f. Phys. Chem., VII., 477, 1889.

formation does not obey the law of van t'Hoff even so well as do copper and tin. The next series of alloys which I tested were of nickel and silver prepared at the University of California. The nickel was melted in a graphite crucible lined with a mixture of calcined magnesia and alumina like that used by Messrs. Allen and Day as insulation in the furnace which they employed to standardize the normal platinum — platinum-10 per cent. rhodium thermocouple,[1] and the formula for which was given me by Dr. Day. The graphite crucibles so lined were found satisfactory. In this way a series of nickel-cobalt alloys were made and two alloys of nickel and silver containing 4 and 8 per cent. of silver respectively. On testing these alloys, the temperature of transformation was found to be 390° C. irrespective of the amount of silver. The permeability of the alloys was found to be lower than that of the nickel, however, by more than the percentage of the silver present.

M. Levin studied a series of nickel-gold alloys with from 0 to 90 per cent. of gold.[2] The temperature of transformation was independent of the amount of gold in the alloy and was near 310° C. The fact that the different specimens of nickel show so widely varying points of transformation is probably due in large measure to the impurity of some of them. The presence of iron or cobalt would raise this temperature slightly while carbon would lower it considerably. For example, the commercial nickel used in my alloys and melted in the lined graphite crucible transformed at 390° C., while a specimen of the same metal which had been melted in the unlined graphite crucible became unmagnetic at 300° C.

Alloys containing equal parts of nickel and gold and of nickel and platinum were found by Lampadius[3] to be as permeable as pure nickel. It may be that in the cases of the nickel-silver and nickel-gold alloys we have to do with mixtures resembling chryohydrates rather than solid solutions.

Osmond, and later Dumas, determined the transformation points of nickel-iron alloys and found that this point rises with the amount of iron till the latter reaches 30 per cent. and then falls again, so that the temperature of transformation may have the same value for

[1] PHYSICAL REVIEW, XIX., p. 177, 1904.
[2] Zeitschr. f. anorgan. Chem., 45, p. 238, 1904.
[3] Wiedemann, "Elektricitaets Lehre," III., p. 784.

two values of the iron content. Dumas tested a small number of alloys of nickel and chromium and of nickel and manganese. 2.7 per cent. of chromium depressed the point of transformation 125°, or 42° per per cent.; 4.3 per cent. depressed it 225°, or 52° per per cent., while greater amounts of chromium did not cause further lowering of the temperature of transformation, indicating probably that the chromium was no longer forming a solid solution with the nickel.

In the nickel-manganese alloys, the depressions of the transformation point were:

Per Cent. Mn.	Depression.	Depression per Per Cent.
3.7	80°	21°
8.8	110	12
13.0	200	15

In both the nickel-chromium and the nickel-manganese alloys, the lowering of the point of transformation is not proportional to the amount of chromium or of manganese in the alloy but is irregular. The alloys of Dumas contained as high as 1.5 per cent. of iron which would vitiate the results.

Alloys of nickel and cobalt were studied by Guertler and Tammann.[1] The transformation point rose regularly from that of nickel to that of cobalt (1100° C.). Moisson[2] prepared borates of iron, cobalt and nickel but the temperatures of transformation were not given, though the compounds were magnetic. Alloys of nickel and antimony were made by K. Lossern.[3]

Metal with Nickel.	Atomic Weight.	Depression per Per Cent.	Observer.
Chromium.	52.1	45° C. Irregular.	Dumas.
Manganese.	55.0	16° C. Irregular.	Dumas.
Iron.	56.0	Point rises.	Osmond-Dumas.
Cobalt.	59.0	Point rises.	Guertler-Tammann.
Copper.	63.6	10.5°. Regular.	Hill.
Silver.	107.9	Independent of alloy.	Hill.
Tin.	118.5	7.3°. Regular.	Hill.
Gold.	197.2	Independent of alloy.	Levin.

[1] Zeitschr. f. anorgan. Chem., 42, p. 353, 1903.
[2] Ann. de Chim. et de Phys. (7), 9, 272, 1905.
[3] Zeitschr. f. anorgan. Chem., 49, p. 58, 1906.

The experimental results already given for the effect of various metals upon the transformation point of nickel are collected in the table.

There appears, then, to be no simple relation between the atomic weights of the metals named in the table and their effect in changing the temperature of transformation of nickel when in alloy with them. As already stated, we probably do not know the molecular weights of the metals at ordinary temperatures. Professor Howe, of Columbia University, says in his book on "Iron, Steel and Other Alloys" that in alloy-steel two parts of molybdenum replace one part of chromium as might be expected from their atomic weights. In the light of the experiments upon nickel alloys just described, I do not think that we can recognize any so general law. In the cases of manganese and chromium alloyed with nickel, a concentration is reached where a further addition of the second metal causes no greater lowering of the transformation point, and with gold and silver this point of saturation, if we may call it so, is reached at a very low concentration if there is a true solid solution of these metals in the nickel at all. It might be of value to know to what extent the properties of the alloy-steels are due to changes in the nature of the iron itself and how much to the nature of the other constituents of the alloy. It is certain that the addition of a small amount of manganese or chromium to steel produces an effect greatly out of proportion to the amount added if we consider the properties of the alloy as in a sense the mean of those of the components. It is only therefore in the most general way and on physical, rather than on chemical grounds, that the properties on an alloy of iron or nickel with any other metal can be predicted. We might expect an alloy to present properties like those of the metals composing it, but this is not necessarily the case as is seen in the copper-aluminium alloys. Both of these metals are soft and ductile but the alloy is very hard and somewhat brittle. It is probable that the properties of any alloy will always have to be found by experiment though some surmises may be made beforehand as to their character.

PHYSICAL LABORATORY,
UNIVERSITY OF KANSAS,
January, 1907.

ROTATION AND ELLIPTIC POLARIZATION PRODUCED BY IRON FILMS IN A MAGNETIC FIELD.[1]

By W. D. Harris.

THE rotation of plane polarized light passing through metallic films in the direction of a magnetic field has been determined by Kundt,[2] DuBois,[3] Lobach,[4] Righi,[5] and others. Righi also discovered that an iron film produced at the same time a small ellipticity in the transmitted ray, which, measured for red light, gave a ratio of $\frac{1}{2}\frac{1}{9}$ for the two axes of the ellipse. Righi's discovery of the effect of iron under the influence of a magnetic field led Cotton[6] to investigate certain optically active solutions for the presence of the same phenomenon, and in these he discovered and measured the ellipticity of the transmitted light. By means of a Brace half-shade elliptic polarizer and compensator McDowell[7] succeeded in extending the work of Cotton considerably. This suggested the possibility of making with the same system a more thorough examination of the elliptic polarization produced by iron films under the influence of a magnetic field. The object of this investigation was primarily therefore to determine the ellipticity produced by iron films as affected by wave length of light and strength of magnetic field; to find the connection, if any, between this and the corresponding rotation of the plane; and to test for ellipticity of the reflected ray, the presence of which theoretical considerations might lead us to expect. The experimental results led finally to a study

[1] Read before joint meeting of the Am. Phys. Soc. and Section B of the A. A. A. S., Ithaca, June, 1906.

[2] Wied. Ann., 23, p. 223, 27, p. 191.

[3] Wied. Ann., 31, p. 941.

[4] Wied. Ann., 39, p. 347.

[5] Mem. R. Accad. Sc. d. Bologna, 1886, p. 443.

[6] L' eclairage Electr., T. 8, pp. 162, 198. Ann. de Chem., et de Phys., Series 7, T. 8, p. 347.

[7] Phys. Rev., XX., p. 293.

of films produced under different conditions, as there were indications that the presence of absorbed gases affected materially the magnitude of the results obtained. In addition to iron, cobalt and nickel films were also tested.

APPARATUS.

Fig. 1 shows the arrangement of the optical system. Sunlight reflected from a heliostät is focused by lens N on slit B placed at

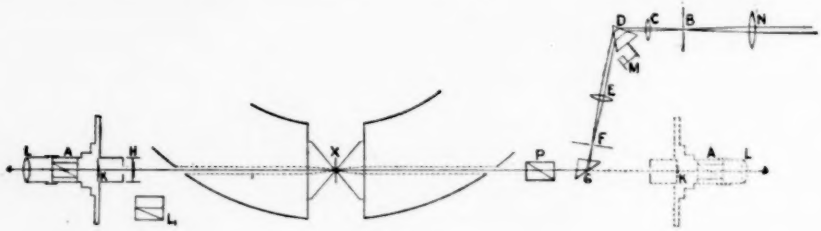


Fig. 1.

the principal focal distance from the achromatic lens C. The colors dispersed by the prism D are focused by E in the plane of the slit F. This light is directed by a total reflecting prism through polarizer P, the film X (placed normal to the field between poles of the magnet), and the half-shade H which is observed by means of the lens L, through the compensator K (mounted on a graduated circle) and analyzer A.

Measurement of Ellipticity.— For adjusting the system, the half-shade and compensator are removed, the polarizer and analyzer "crossed"; then the half-shade (an exceedingly thin strip of mica) is placed to cover half the field and so that its principal plane makes an angle of 45° with the plane of polarization, as indicated by maximum intensity. The compensator K (also a thin strip of mica, of about twice the order of the half shade) is next introduced (covering the entire field) and this rotated to produce a match of intensity in the two halves of the field. A small ellipticity produced in the originally plane polarized light is then measured as proportional to the angle through which the compensator must be rotated to reproduce the match. The order of the one used is given by McDowell as 1/40 for yellow-green light [1]). By rotating the compensator

[1] Since Righi used for this purpose a quarter wave plate, the system employed here should, for the same ellipticity, give about ten times the rotation he observed, namely, 2.5° where he had 15′. As may be seen by referring to curve H, Fig. 3, this magnitude was obtained with films deposited in hydrogen.

from a "match" through 0.1° a marked contrast in the two parts of the field became evident. When, as in the present case, the medium tested produces also a small rotation, the polarizer may first be rotated to produce minimum intensity of field — the condition for maximum sensibility — after which the compensator is set for a match, the angle through which it is rotated being a measure of the ellipticity as before.

Measurement of Rotation. — To measure the rotation of the plane of polarization, the half-shade and compensator were removed while the analyzer *A* combined with a Lippich prism *Li* was mounted in the graduated circle. With good light a rotation of 0.05° could readily be detected by destroying the "match" of the two halves of the field of view. In the observations with films a variation of more than 0.1° from the mean of several was unusual except in the violet where the intensity of the transmitted light was very low.

The Electromagnet.—This consisted (Figs. 1, 2) of two semi-circular cores (forming a circle about 56 cm. in diameter), wound uniformly over the whole length with 110 pounds of No. 14 magnet wire. Two accurately planed soft iron wedges *O* and *S*, Fig. 2, permitted the distance between pole pieces to be varied with ease. Cold water circulating through a hollow copper tube wound next to the core reduced the heating when working with the higher currents.

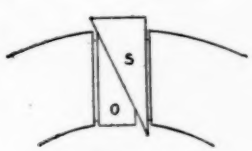


Fig. 2.

Two sets of pole pieces were provided, one pierced by an aperture of one millimeter diameter, and the other five. With the former a current of 1 ampere gave through an air gap of 3.3 millimeters a field strength of 10,000 C.G.S. units; 8.5 amperes, 15,000; 23 amperes, 17,000. By using the pole pieces of smaller aperture with a shorter air gap a much stronger field could be produced, but this proved unnecessary in the present work. The field strength was determined by the rotation it produced in a tube of carbon bisulphide of given length, its value being calculated from Verdet's constant as determined by Rayleigh.

A 500-volt power circuit furnished the higher currents, a storage battery the smaller. Suitable rheostats permitted the current to be varied by steps up to 24 amperes.

PRODUCTION OF FILMS.

Righi used a film deposited by the electrolysis of ferrous ammonium sulphate on half-silvered glass. Kundt used the same solution, depositing on platinized glass. He also deposited by a cathode discharge in vacuo.

All films used in this investigation were deposited from the cathode under the glow discharge after the manner of Wright,[1] Longdon,[2] Kundt,[3] Patterson[4] and others. This was done with a gas pressure of less than a millimeter of mercury and a current of about 25 milliamperes furnished by a small 1,000-volt generator. The character of the deposit varied greatly with the distance of the plate from the cathode and some practice was necessary to obtain a metallic mirror deposit of sufficiently uniform thickness, this being necessary since an irregular or prismatic film may exhibit double refraction as pointed out by Kundt.[5] The most satisfactory distance from the cathode was found to be 2 or 3 millimeters outside the Crooke's dark space.

Iron films were deposited in hydrogen, nitrogen and oxygen. Only those with even mirror surface were used. Films deposited in hydrogen and nitrogen show by transmitted light a dark seal brown color when thin and transparent, and a steel gray appearance when translucent. Those in oxygen appeared a distinct reddish brown.

As the success of the experiment depended on the purity of the deposit, much care was exercised in eliminating impurities in the cathode. The best grade of soft Swedish iron, terminating in a circular disc of 2 millimeters diameter was used.

To remove the foreign gases givenoff during action, the discharge tube was washed out repeatedly with the gas used during the deposition. Before starting the current the system was allowed to stand in connection with a phosphorus pentoxide dryer to remove any water vapor present. Thin sections of the fresh films obtained in the different gases exhibited strong polarity when suspended by silk fibers

[1] Am. Jour. Science, XIII., pp. 49–169, 1877.
[2] PHYS. REV., XI., pp. 40–84.
[3] Wied. Ann., 27, p. 59.
[4] Phil. Mag., 4, p. 652.
[5] Wied. Ann., 27, p. 59. [The effect of lack of uniformity could, however, be obviated to a large extent by confining observations to a small area of sufficient evenness.]

in a magnetic field, while the older ones showed it but feebly if at all. The difference was ascribed to gradual oxidation of the films after exposure to the atmosphere, since after a time all trace of both magnetic rotation and ellipticity disappeared. Nickel and cobalt films deposited from chemically pure cathodes were also obtained by the same process.

Preliminary Trials.

As the ellipticity produced by iron was known to be very small and perhaps peculiar to the manner of deposition used by Righi, various refinements in method were at first attempted, to eliminate, if possible, all factors but that arising from the iron alone.

Since the glass on which the films are deposited may become doubly refracting by the heat during process of deposition, the effect increasing with the thickness, the plan was tried of mounting very thin films of blown glass on small glass frames and depositing the film of metal on the thin section of glass. This method proved unsatisfactory. The plan was also tried of depositing the metal on different polished crystals and then by dissolving the crystal leave the metal film to be mounted, but, though iron is very tenacious ordinarily, films could not be obtained thin enough to be transparent and yet strong enough to be mounted. Finally thin microscope coverglasses, selected free from double refraction before deposition and then with part of the film removed by acid, also tested after deposition, were found to work very satisfactorily. Although in a nearly saturated field these produced a rotation of the plane large enough to be detected, yet it was smaller than the fluctuation in observations made on the film, and hence ignored in the results.

Another scheme was tried with the hope of eliminating the platinized surface of Kundt's and the silvered of Righi's experiment. This was to deposit first the exceedingly thin conducting layer of iron on the glass by the cathode method, and use this to deposit films electrolytically with the Varrentrap bath method, but no satisfactory films could be obtained.

The first iron films tested had been deposited in nitrogen a few months before. They revealed no ellipticity though a very small rotation not caused by the glass was present. These films imparted to transmitted light the reddish brown tint of the oxide rather than

that of metallic iron. In order to avoid oxidation, films were therefore deposited in an atmosphere of hydrogen and left in this until they could be removed for an immediate test. These were found to possess to a marked degree the power of producing both rotation and elliptic polarization, thus indicating that the same was destroyed in the old films probably by oxidation. In fact, as will be shown, these films gradually though slowly lost these properties.

STUDY OF IRON.

Films Deposited in Hydrogen. — Fresh films, deposited in hydrogen, were now tested for the rotation and ellipticity produced on various wave-lengths of transmitted light in a magnetic field of definite intensity. These films were as thick as was consistent with reliable measurements.

In Table I. are recorded two series of such observations taken on successive days with a film which had been left unchanged in its position during that time.[1] The strength of field was about 7000 C.G.S. units; such as to produce a nearly maximum ellipticity.

TABLE I.

Film Deposited in Hydrogen. Strength of Field, 7,000 *C.G.S.*

Wave-Length.	First Series.		Second Series.	
	Rotation.	Ellipticity.	Rotation.	Ellipticity.
466 $\mu\mu$	0°	.03°	0°	.12°
521	0.21	1.98	0.22	2.00
537	—	2.29	—	2.34
550	0.47	—	0.40	—
556	—	2.88	—	2.88
561	0.46	—	0.42	—
603	0.62	—	0.65	—
612	—	3.00	—	2.97
621	0.68	2.89	0.64	2.90
644	—	2.84	—	2.83
657	0.75	2.67	0.76	2.45
684	0.84	2.50	0.82	2.41
712	0.84	2.20	0.82	2.20

[1] It proved to be a difficult matter to return a film, after removal, to its original position with sufficient accuracy to reproduce observations within the limits of error of the optical settings, although it was carefully diaphragmed down to the size of the aperture in the pole-pieces.

The fluctuation in the observed values was generally largest at both extremities of the spectrum where the absorption was greatest, but this error was in part compensated for by making a larger number of settings for a given wave-length. In all cases the double value was obtained by reversing the magnetic field; however, only the single values are recorded.

The results in Table I. are represented graphically by curves *H* in Fig. 3, the upper plot indicating the rotation of the plane of

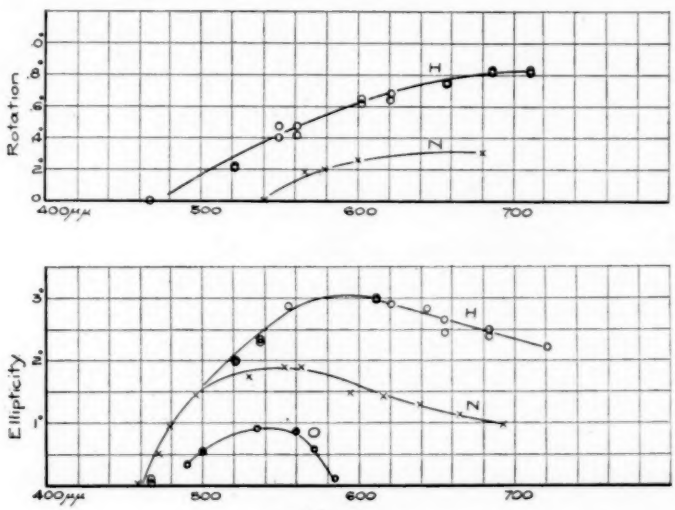


Fig. 3.

polarization with wave-length, and the lower the amount of elliptic polarization produced (in terms of the rotation of the compensator).

Comparing the rotation here with that given by Lobach (*l. c.*), it is noted that in agreement with his values it is anomalous, *i. e.*, it increases with wave-length; but though he observed that the rotation for a wave-length of 430 $\mu\mu$ was about half that for 670 $\mu\mu$ the value here drops to practically zero at about 470 $\mu\mu$. While the accuracy of the settings in this region is not at all good, yet these values were obtained repeatedly by two observers, so that we are led to believe in their correctness. The curve here is also distinctly concave toward the axis of abscissas, while that of Lobach approaches closely to a straight line. In the main, however, the rotation of the plane in this case indicates that we have to do with a normal iron film.

The ellipticity of the transmitted light, given in the lower plot, rises rapidly from a zero value, at the same wave-length as the curve of rotation, 470 $\mu\mu$, to a maximum at about 590 $\mu\mu$ and then drops slowly towards the red end of the spectrum. The point of maximum ellipticity lies in the yellow-green part of the spectrum, which qualitative tests with a spectroscope showed was also the region of least absorption.

When compared with results given by optically active solutions in which an absorption region is present, *the ellipticity produced by iron also appears anomalous*, in the sense that, as shown by Cotton and by McDowell, the latter reveal a maximum ellipticity in the region of greatest absorption.

Films Deposited in Nitrogen. — As stated above the first films tested had been deposited in nitrogen some time previously. The fresh films from hydrogen revealed such a marked increase in action over the old that it was questionable if this arose entirely from age. To test this, films were deposited in nitrogen and subjected to an immediate test. Table II. represents the results obtained from one

TABLE II.

Film Deposited in Nitrogen. Strength of Field, 12,000 *C.G.S.*

Wave-Lengths.	Rotation.	Ellipticity.	Wave-Lengths.	Rotation.	Ellipticity.
458 $\mu\mu$	—	0.03°	564 $\mu\mu$	—	1.90°
464	0.10°	—	567	0.18°	—
473	—	0.52	579	0.20	—
479	—	0.95	595	—	1.48
496	—	1.45	600	0.23	—
500	—	1.50	616	—	1.43
503	Trace.	—	639	—	1.31
512	Trace.	—	664	—	1.23
530	—	1.73	680	0.30	—
538	Trace.	—	693	—	0.94
553	—	1.92			

(caused by the glass.)

of these which to all appearances did not differ from that obtained with hydrogen. It appeared equally susceptible to magnetism and absorbed about the same amount of light.

The rotation produced by this film in a magnetic field of 12,000 C.G.S. units is represented by the curve *N* in Fig. 3, upper plot;

and the ellipticity by N in the lower plot. The rotation is less than half that of the hydrogen film — starting from a zero value at about 540 $\mu\mu$ and rising to about a constant maximum between 600 and 680 $\mu\mu$. The ellipticity rises from a zero value at the same point as the hydrogen film, reaches a smaller maximum value at about 560 $\mu\mu$ instead of 590, then drops to a value less than half that of the hydrogen film at 690. On comparing the two films for transmitted light by a spectroscope, the absorption at the extremities of the spectrum appeared somewhat greater in the nitrogen film, than in the one deposited in hydrogen.

Films Deposited in Oxygen. — Films deposited in oxygen were next tested in a magnetic field of the strength used in the previous case, 12,000 units. A film was chosen of about the same optical density as the others and tested, as before, for both rotation and ellipticity. Only a trace of rotation could be detected and this increased with decreasing wave-length, which indicated that the effect was caused by the glass and not the film. A measurable ellipticity was however present. This is given in Table III. and represented by

TABLE III.

Film Deposited in Oxygen. Strength of Field, 12,000 *C.G.S.*

Wave-Length.	Ellipticity.	Wave-Length.	Ellipticity.
490 $\mu\mu$	0.33°	572 $\mu\mu$	0.60°
500	0.55	585	0.10
535	0.90	600	Trace.
560	0.84	705	No trace.

curve O in the lower plot of Fig. 3. The ellipticity rises from a zero value very likely in the same vicinity as the other curves, but owing to the great absorption in this region by the oxygen film no observation there could be made. The maximum value of this curve compared with the others appears to be shifted toward the shorter wave-lengths, and possesses a magnitude only about half that of the nitrogen film. The curve drops comparatively rapidly also toward a zero value at about 590 $\mu\mu$. This film absorbed much more light at both ends of the spectrum than either of the others giving to transmitted light a very different tint. Here, too, the

The ellipticity of the transmitted light, given in the lower plot, rises rapidly from a zero value, at the same wave-length as the curve of rotation, 470 $\mu\mu$, to a maximum at about 590 $\mu\mu$ and then drops slowly towards the red end of the spectrum. The point of maximum ellipticity lies in the yellow-green part of the spectrum, which qualitative tests with a spectroscope showed was also the region of least absorption.

When compared with results given by optically active solutions in which an absorption region is present, *the ellipticity produced by iron also appears anomalous*, in the sense that, as shown by Cotton and by McDowell, the latter reveal a maximum ellipticity in the region of greatest absorption.

Films Deposited in Nitrogen. — As stated above the first films tested had been deposited in nitrogen some time previously. The fresh films from hydrogen revealed such a marked increase in action over the old that it was questionable if this arose entirely from age. To test this, films were deposited in nitrogen and subjected to an immediate test. Table II. represents the results obtained from one

TABLE II.

Film Deposited in Nitrogen. Strength of Field, 12,000 *C.G.S.*

Wave-Lengths.	Rotation.	Ellipticity.	Wave-Lengths.	Rotation.	Ellipticity.
458 $\mu\mu$	—	0.03°	564 $\mu\mu$	—	1.90°
464	0.10°	—	567	0.18°	—
473	—	0.52	579	0.20	—
479	—	0.95	595	—	1.48
496	—	1.45	600	0.23	—
500	—	1.50	616	—	1.43
503	Trace.	—	639	—	1.31
512	Trace.	—	664	—	1.23
530	—	1.73	680	0.30	—
538	Trace.	—	693	—	0.94
553	—	1.92			

caused by the glass.

of these which to all appearances did not differ from that obtained with hydrogen. It appeared equally susceptible to magnetism and absorbed about the same amount of light.

The rotation produced by this film in a magnetic field of 12,000 C.G.S. units is represented by the curve *N* in Fig. 3, upper plot;

and the ellipticity by N in the lower plot. The rotation is less than half that of the hydrogen film — starting from a zero value at about 540 $\mu\mu$ and rising to about a constant maximum between 600 and 680 $\mu\mu$. The ellipticity rises from a zero value at the same point as the hydrogen film, reaches a smaller maximum value at about 560 $\mu\mu$ instead of 590, then drops to a value less than half that of the hydrogen film at 690. On comparing the two films for transmitted light by a spectroscope, the absorption at the extremities of the spectrum appeared somewhat greater in the nitrogen film, than in the one deposited in hydrogen.

Films Deposited in Oxygen. — Films deposited in oxygen were next tested in a magnetic field of the strength used in the previous case, 12,000 units. A film was chosen of about the same optical density as the others and tested, as before, for both rotation and ellipticity. Only a trace of rotation could be detected and this increased with decreasing wave-length, which indicated that the effect was caused by the glass and not the film. A measurable ellipticity was however present. This is given in Table III. and represented by

TABLE III.

Film Deposited in Oxygen. Strength of Field, 12,000 *C.G.S.*

Wave-Length.	Ellipticity.	Wave-Length.	Ellipticity.
490 $\mu\mu$	0.33°	572 $\mu\mu$	0.60°
500	0.55	585	0.10
535	0.90	600	Trace.
560	0.84	705	No trace.

curve O in the lower plot of Fig. 3. The ellipticity rises from a zero value very likely in the same vicinity as the other curves, but owing to the great absorption in this region by the oxygen film no observation there could be made. The maximum value of this curve compared with the others appears to be shifted toward the shorter wave-lengths, and possesses a magnitude only about half that of the nitrogen film. The curve drops comparatively rapidly also toward a zero value at about 590 $\mu\mu$. This film absorbed much more light at both ends of the spectrum than either of the others giving to transmitted light a very different tint. Here, too, the

maximum ellipticity was evidently in the region of least absorption.

The results from the films deposited in the different gases leads to the interesting question as to how the gas affects the qualities of the film. As with the others, the oxygen film showed magnetic susceptibility, yet it is probable that much of it was in reality an oxide of iron. It is very likely also that a certain amount of nitrogen combined with the iron during the process of deposition in that gas, as a continuous decrease of gas pressure was noted, though this may have arisen from anode absorption.[1] As to whether the film deposited in hydrogen was free from any effect arising from the presence of absorbed hydrogen[2] remains at present an open question, as the writer was unable to carry the investigation farther.

Deterioration of Hydrogen Films. — In Table IV. are given com-

TABLE IV.

Showing Deterioration of Film Deposited in Hydrogen. Field Strength, 7,000 *C.G.S.*

Wave-Length.	Ellipticity.		Wave-Length.	Ellipticity.	
	Fresh Film.	Same, 1 Month Later.		Fresh Film.	Same, 1 Month Later.
470 $\mu\mu$	0°	—	621 $\mu\mu$	—	2.60°
504	—	1.81°	626	2.80	—
524	1.98	—	632	—	2.48
535	—	2.40	642	—	2.48
538	2.30	—	650	2.78	—
561	—	2.64	658	2.65	2.03
567	2.80	—	687	—	1.59
589	—	2.79	691	2.49	—
612	3.00	2.64	712	2.20	1.58

parative results of the ellipticity produced by a fresh film deposited in hydrogen and the same film tested a month later. The observations were made with a magnetic field of about 7,000 units. The results are plotted as before in Fig. 4. Curve H represents those from the fresh film, H' those from the same film one month later. It is evident that with age the qualities of the hydrogen film approach those of the nitrogen and oxygen films, the change being greater with the longer wave-lengths.

[1] See Skinner, PHYS. REV., XXI., p. 169.

[2] W. Heald (PHYS. REV.) has found that freshly deposited iron absorbs a considerable amount of hydrogen at pressures as low as those used in this work.

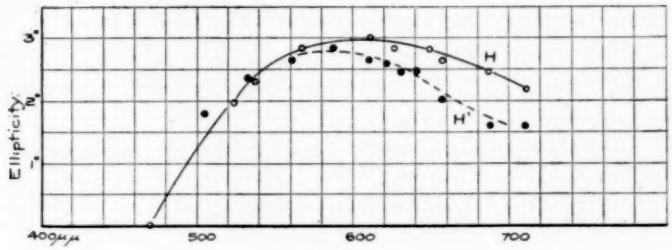


Fig. 4.

Variation of Ellipticity with Intensity of Field. — In Table V. are

TABLE V.

Ellipticity with Strength of Field.

Field Intensity (C. G. S.).	Ellipticity.	Field Intensity (C. G. S.).	Ellipticity.
3,000	1.09°	13,400	3.15°
5,600	2.11	13,950	3.18
9,800	3.03	14,300	3.22
12,000	3.13		

recorded the results of observations of the ellipticity produced on a wave-length of 548 $\mu\mu$ by a film deposited in hydrogen, in a magnetic field of different intensities. The film used was the one which served for the results given in Table I. Fig. 5 gives a graphical

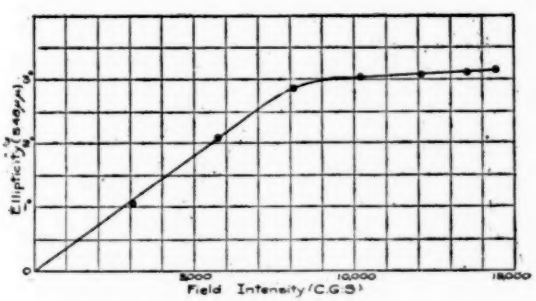


Fig. 5.

representation of the same, in which the abscissas represent the field strength and the ordinates the corresponding ellipticity it produced. The curve shows that up to an intensity of about 7,000 the ellipticity is proportional to the intensity, but beyond that the rate of increase quickly drops to a very small quantity. Its form is similar

to that given by Kundt's results (l. c.) on the rotation of the plane under similar conditions.

Test of Reflected Light. — Righi suggested that the ellipticity of the transmitted light arises from the unequal reflecting power of the iron for the two opposite circular vibrations into which the incident plane vibration is resolved. To test this theory the observing system was removed to the opposite side of the film (position dotted in Fig. 1) and the reflected light observed under the same conditions as the transmitted had been. With a film which produced most marked ellipticity in the transmitted ray, repeated observations, with the strongest fields and the best of light, revealed no ellipticity of the reflected ray. The test was made under conditions such that a rotation of 0.1° of the compensator produced a very clear change in the relative intensity of the two parts of the field of view. A test of the transmitted component required a rotation of the compensator of about 6° to reproduce a match on reversing the field. If on account of large absorption in the film the effect on reflection from the front surface only be taken into account, there should have been an ellipticity in the reflected light of half that observed in the transmitted, or a rotation of the compensator of 3° should have been required to reproduce a match after reversing the magnetic field. This was however certainly less than 0.1°. Hence it is to be concluded that the ellipticity arises from unequal absorption of the two circular components in passing through the film rather than from unequal reflection at its surfaces.

TEST OF NICKEL AND COBALT FILMS.

Both nickel and cobalt films deposited in nitrogen were tested for ellipticity of the transmitted light under the same conditions as iron. Though films of these metals produce a rotation of the plane in a magnetic field, no ellipticity of either transmitted or reflected light could be detected for any color, under the best working conditions. The films tested were optically as dense as the iron.

The writer is indebted to the late Dr. Brace under whose direction this research was undertaken, and to Dr. C. A. Skinner for assistance which made its completion possible.

THE BRACE LABORATORY OF PHYSICS,
UNIVERSITY OF NEBRASKA, LINCOLN.

THE PERCENTAGE BRIDGE.

By A. C. Longden.

ABOUT six years ago, a paper entitled "A Percentage Bridge" was presented to the American Institute of Electrical Engineers by Mr. Herschel C. Parker, of Columbia University.

The method which this paper advocated does not seem to me to have received the recognition which it deserves. It may be partly because we are satisfied to "let well enough alone," and partly because of the position of commanding authority occupied by the Carey-Foster method. Be that as it may, the conclusion has been gradually forced upon me, as I have been using the two methods during the past few years, that the Percentage Method, with a few modifications is in no way inferior to the Carey-Foster method, and that it is in some ways a little the better method.

The percentage bridge may be briefly described as an ordinary four gap slide wire bridge, such as is shown in Fig. 1, in which the auxiliary resistances A_1 and A_2 are equal, and have such a relation to the resistance of the bridge wire that a change of one hundredth of 1 per cent. in the ratio of R_1 to R_2 shall produce a change of one millimeter in the position of the balancing point, p, on the bridge wire.

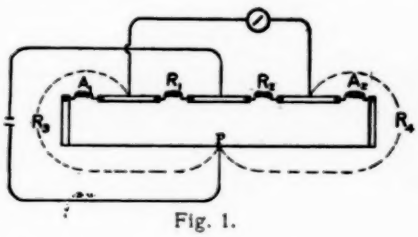


Fig. 1.

In using the bridge, one of the resistance gaps, R_1 for example, is used as the substitution gap. A standard resistance is placed in this gap and balanced against R_2. R_2 should be approximately equal to R_1, so that the balancing point shall be at or near the middle of the bridge wire. The exact value of R_2, however, does not need to be known. When the bridge is balanced, the test coil is substituted for the standard in the substitution gap. If this disturbs the balance,

the bridge is again balanced and the distance in millimeters on the bridge wire between the two balancing points indicates the difference of resistance in hundredths of 1 per cent., between the test coil and the standard. If the slider is provided with a vernier, so that its movements can be read in tenths of millimeters, these readings correspond to differences in thousandths of 1 per cent.

This method, aside from its usefulness in standardizing rheostats, has a number of real advantages over the Carey-Foster method for comparing standard resistance units. Mr. Parker says: "For the comparison of standard resistance units of the same value, the Carey-Foster method, using the 'commutator Bridge,' furnishes a very precise and satisfactory means of measurement." Later, however, he refers to the simplicity of the Percentage Bridge, with its four mercury cups, as compared with the complicated commutating device of the Carey-Foster bridge, with its twenty mercury cups. This is a hint which I think we ought to take, for I fear we sometimes rely upon our measurements because we made them with the Carey-Foster bridge, when they are really not as reliable as we suppose. The fact that we cannot repeat them with the degree of precision which the theory of the method warrants, if we use another bridge, or even sometimes with the same bridge, ought to be evidence that there is room for a suspicion that something is wrong. The simplicity of the percentage method and of the apparatus used in connection with it, ought at least to entitle it to a serious consideration.

Two of the strongest points in favor of the Carey-Foster method are that the resistance of the end connections of the bridge is eliminated, and that the coils may be interchanged without handling them. The importance of the first of these claims is considerable when the bridge is used in the ordinary way and when all of the resistances in the bridge circuit are low; but when the end resistances amount to as much as twenty ohms each, as they usually do in the percentage bridge, the importance of exact equality of the end connections is not as great. Suppose, for example, the resistance of one of the end connections should exceed that of the other by one hundredth of an ohm, and this is an inexcusably large excess, even then the *difference* is only one twentieth of one per cent.,

and the error in the *result* of the measurement is only one twentieth of one per cent. of one hundredth of one per cent., or one part in twenty million for each millimeter of the bridge wire! Of course, it is needless to say that such an error is quite negligible even in measurements of the highest attainable precision. It is evident then, that spurious resistances which would be fatal to success in the Carey-Foster method, if not eliminated, are quite negligible when the percentage method is used.

The other claim, that the coils may be interchanged without handling, has, I am inclined to believe, lost much of its importance with recent improvements in the construction of resistance standards. The Carey-Foster commutator was invented when the British Association form of resistance standard was the only one in vogue. When the wire of which the coil was made was securely packed away in a thick mass of heat insulating material in order that changes of temperature might be retarded as much as possible, it was important that the coils to be compared should be placed in oil baths several hours before the final tests were made; and it was equally important that they should not be disturbed during the tests. The present method of constructing resistance coils requires that the wire shall be exposed to the oil as fully as possible, so that a coil at any temperature, within reasonable limits, may be placed in an oil bath and it will assume the temperature of the oil in a few minutes. The only important change resulting from such a course will be a slight change in the temperature of the bath; and as this can be easily determined and readjusted, the matter is not at all serious. Furthermore, the temperature of the coil may be brought to the temperature of the bath by means of an auxiliary bath, so that no perceptible change of temperature need occur when one coil is substituted for another. It must also be remembered that even if the temperature of the bath be changed, it is perfectly legitimate to compare the resistance of a test coil at one temperature with the resistance of a standard at another, and finally, it must also be remembered that the case to which I have referred is an extreme one. It is far more likely that the two coils will be in oil baths at the same temperature, or perhaps they will be in the same bath. Of course, it is important that the conducting rods and the metal parts of the mountings should not be heated by contact with the hand.

I am not arguing that it is just as well to handle the coils as not to handle them, but I do argue that the importance of the matter is not as great with the Reichsanstalt form of coil as with the B. A. form. I will also add that if the interchange without handling requires a commutator with twenty mercury cups, the operation is at least questionable.

If it is really important to substitute one coil for another without moving or touching the coils, this can be accomplished much more easily in the percentage bridge than in the Carey-Foster bridge. It is only necessary to extend the terminals of the substitution gap a short distance, as at A, in Fig. 2, placing a copper block carrying three small mercury cups or one large one at B. The two coils to be compared, R_x and R_s may then be placed side by side in the same oil bath and may remain undisturbed, and either one of them may be short circuited by means of the heavy copper loop, L, while the other is being balanced against R_2. The resistances of the loop and of the extension bars may be very small, but it is not necessary that they should be negligible for they do not enter into the measurement at all, as the substitution occurs at their extremities.

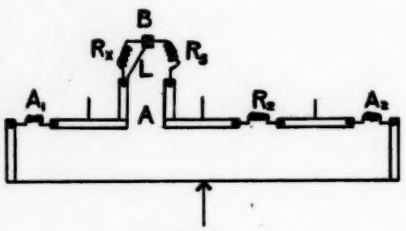


Fig. 2.

Another distinct advantage of the percentage method is its sensitiveness. In the Carey-Foster bridge, the bridge wire must be comparatively large, in order that small differences of resistance may be easily detected and measured. Of course, there is no special reason why the wire should *not* be large, except that a large wire means a small *range;* but there must be a limit somewhere, beyond which we could scarcely expect to go. It may be said in general, whatever the size of the wire, that with the same bridge wire, the same galvanometer and the same current flowing through the standard coils, it is about as easy to measure thousandths of one per cent. with the percentage bridge as to measure hundredths of one per cent. with the Carey-Foster bridge.

The auxiliary coils A_1 and A_2 in Fig. 1, not only serve the pur-

pose of adjusting the percentage ratio to one hundredth of one per cent., but, having a resistance of about twenty ohms each, they protect the standard coils from heavy currents, making it unnecessary to introduce added resistance into the battery circuit, outside of the bridge circuit, as is done in measuring low resistances by the Carey-Foster method.

The battery and galvanometer should be arranged as in Fig. 1, connecting one of the battery wires between R_1 and R_2 and the other to the slider. This puts the auxiliary coils in series with the standard coils and also with the bridge wire, protecting the entire system of standard resistances.

Another advantage of the percentage bridge which is at least worth mentioning, is its range. As has already been remarked, the Carey-Foster bridge is an instrument of low range, usually one per cent. or less, because of the low resistance of the bridge wire. In the percentage bridge adjusted to a percentage ratio of one hundredth of one per cent. per millimeter, the range, for a bridge having a wire a meter long, is ten per cent., minus a small fraction of each end of the wire, upon which the slider cannot be operated.

One of the special fields in which the percentage bridge is very useful and exceptionally convenient is the measurement of temperature coefficients. It is not necessary to compare the resistance under test with a standard or even to know its resistance at all. It is simply placed in the substitution gap and balanced against R_2. Its temperature is then changed and a new balance obtained. Since the distance in millimeters between the two balancing points on the wire is numerically equal to the change in resistance in hundredths of one per cent., it is only necessary to read this distance and divide it by the change in temperature in degrees to obtain the temperature coefficient.

The real object of this paper is yet to be stated. I have thus far considered only the virtues of the percentage bridge. It has *one* fault, — just one I think. It is the purpose of this paper to point out the fault and to present a simple method of eliminating the errors resulting from it.

If the auxiliary resistances have such a relation to the resistance of the bridge wire that a change of one hundredth of one per cent. in the ratio of R_1 to R_2, produces a change of one millimeter in the

position of the balancing point on the bridge wire *at any stated position*, this will not be strictly true at any other position. Mr. Parker has taken an *average* value for the ratio of the resistance of the auxiliary coils to that of the bridge wire, and has assumed that it is a sufficiently close approximation for all positions of the slider. He states the value of this ratio as 19.6 to 1. That is, the resistance of each auxiliary coil must be 19.6 times the resistance of the bridge wire. Now as a matter of fact, if the bridge is balanced exactly in the middle, this ratio should be 19.5 to 1. It is 19.6 to 1 if the balancing point is ten centimeters from the middle of the wire.

It is quite obvious that for a small range near the middle of the wire, the errors arising from Mr. Parker's assumption are not very large, but it is also quite obvious that this is true only for a very small range, and that the results are strictly correct, only when the bridge is balanced at a point ten centimeters from the middle of the wire. The errors may, as Mr. Parker suggests, be minimized by adding compensating resistances to the auxiliary resistances when the balancing point is a considerable distance from the center. This, of course, means different ratios for all different positions of the slider.

Instead of thus complicating the apparatus and only *minimizing* the errors, we propose that the errors be wholly eliminated by using a single set of auxiliary coils, correct for the middle point on the wire, and applying a suitable scale of corrections for other points. The following table furnishes the corrections, worked out for points ten centimeters apart on the wire.

A	*B*	*C*	*D*
10cm toward R_4	$\frac{201}{199}$, or 101.005%	1%	.005%
20 "	$\frac{202}{198}$, or 102.020	2	.020
30 "	$\frac{203}{197}$, or 103.046	3	.046
40 "	$\frac{204}{196}$, or 104.082	4	.082
50 "	$\frac{205}{195}$, or 105.128	5	.128
10cm toward R_3.	$\frac{199}{201}$, or 99.005	1	.005
20 "	$\frac{198}{202}$, or 98.020	2	.020
30 "	$\frac{197}{203}$, or 97.044	3	.044
40 "	$\frac{196}{204}$, or 96.078	4	.078
50 "	$\frac{195}{205}$, or 95.122	5	.122

In column A, is found the balancing point on the bridge wire, and in column B, the true ratio of the test coil to the standard for that balancing point. Column C presents the uncorrected difference

between the test coil and the standard, assuming each millimeter of the wire as .01 per cent. The corrections are given in column D.

These corrections are a trifle larger for points on the half of the wire running toward R_4 than for corresponding points on the other half; R_1 being the substitution gap. This is because in that case the ratio of R_3 to R_4 increases as the balancing point runs toward R_4.

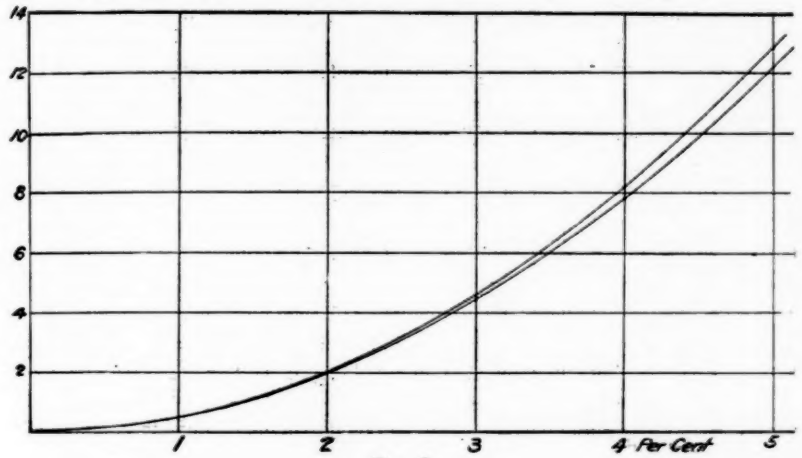


Fig. 3.

Fig. 3 presents curves from which may be taken the correction for any point on the wire. The uncorrected differences in column *C*, are plotted as abscissæ and the corrections in column *D*, as ordinates. The upper curve is for the first half of the table and the lower curve for the second half. A mean between the two would be within .003 per cent. of either, even at the extremities of the wire, where the errors are maximum. The corrections are given in hundredths of one per cent. and are to be *added* to the uncorrected results, using the upper curve, if the bridge readings run toward R_4, and the lower curve, if the readings run toward R_3; R_1 being the substitution gap.

With these corrections properly applied, the percentage method of comparing standard resistances becomes a precision method of the highest rank.

I have said nothing about errors due to the irregularities in the bridge wire, but of course the wire may be calibrated for the percentage bridge as well as for any other.

KNOX COLLEGE PHYSICAL LABORATORY,
GALESBURG, ILL., November 23, 1906.

A SPECTRO-PHOTOMETRIC STUDY OF THE ABSORBING POWER AND THE FLUORESCENCE OF RESORUFIN.

BY FRANCES G. WICK.

IT has frequently been observed that the color of the light emitted by a fluorescent solution is altered by a change in the concentration of the solution. A dilute solution of fluorescein, for example, gives a green fluorescence, while the light emitted by a concentrated solution of the same substance shows a distinctly yellow tinge. In other words an increase in concentration causes the maximum of the fluorescence spectrum to shift toward the longer wave lengths.

Such a shift might result from a real change in the period of vibration of the fluorescent molecules, *i. e.*, the form of the typical fluorescence spectrum might depend upon the concentration of the solution. But the observed change in the fluorescence spectrum might equally well result from a change in the absorbing power of the solution. The light emitted by portions of the active substance in the interior of the solution must pass through the solution before emerging, and is therefore weakened by absorption. Since the maximum of the fluorescence spectrum does not occur at the same wave length as the maximum absorption, being always slightly displaced in the direction of the longer waves, it is clear that different portions of the fluorescence spectrum will be affected by absorption in varying degree; the shorter waves will always be absorbed most strongly. The maximum of the fluorescence spectrum is therefore always shifted toward the red to some extent, and the increased absorbing power of concentrated solutions causes the shift due to this cause to increase with the concentration.

The experiments described in the present paper, the object of which was to determine whether the typical fluorescence spectrum changes with the concentration or whether the shift referred to

above is caused by absorption only, were undertaken at the suggestion of Professors Nichols and Merritt, to whom the author wishes to acknowledge her indebtedness. To their advice and kindly criticism is due whatever may be of value in the results.

The substance used was resorufin, whose strong fluorescence in the yellow-red is conveniently excited and readily observed. The experimental work naturally falls under three heads as follows:

1. The relation between absorption and thickness, to test whether or not the absorption of a fluorescent solution obeys the exponential law of optically perfect substances.

2. The relation between absorption and concentration, to test the application of Beer's[1] law, *i. e.*, that an increase in the concentration of a solution is equivalent to an increase in thickness.

3. The fluorescence spectra of six dilutions of resorufin were observed to determine whether or not there is any shift in the maximum of fluorescence as concentration changes.

The first and second of the problems under consideration have been investigated, to some extent, by B. Walter[2] and by Nichols and Merritt.[3] The results here given for resorufin are entirely consistent with those obtained by these authors for other substances.

Historical.

The history of the investigations upon fluorescence, as related to the above problems, is briefly as follows:

In 1888 B. Walter,[4] using the Vierordt spectrophotometer, found that the ratio of the fluorescent light emitted to total incident light absorbed, Fl/A, increases with dilution. This law had been previously conjectured by Lommel,[5] whose mathematical theory Walter[6] used in verifying his own results. In connection with this work Walter tested Beer's[7] law of absorption for fluorescein by four measurements. He found the law to hold true for dilute but not for concentrated solutions.

[1] Beer, Pogg. Ann., 86, p. 78.
[2] B. Walter, Wied. Ann., 34, 1888.
[3] Nichols and Merritt, Studies in Luminescence, PHYSICAL REVIEW, Vols. 18–21.
[4] B. Walter, Wied. Ann., 34, 1888.
[5] Lommel, Pogg. Ann., 160, p. 76, 1877.
[6] B. Walter, Wied. Ann., 36, p. 502, 1889.
[7] Beer, Pogg. Ann., 86, p. 78.

Walter briefly states his conclusions as follows; "Ability to excite fluorescence, Fl/A, in the most concentrated solutions, is infinitely small or zero. After Fl/A obtains a measurable value it increases in proportion to dilution to a certain dilution called the 'critical point.' For greater dilutions Fl/A remains constant."

In explanation of the above, Walter[1] advances a molecular group theory which is of interest, preceding as it does, the present theory of ionization given by Buckingham.[2] Walter summarizes his theory in the following statements:

1. Every separate molecule of a given substance in solution absorbs, so long as it remains in the separate condition, the same fraction of the light falling upon it no matter how great its distance from other molecules in the solution may be.

2. Every separate molecule of a given fluorescent substance in solution, so long as it is in the separate condition, changes the same fraction of absorbed light into fluorescent light, no matter how great its distance from neighboring molecules may be.

3. As soon as molecules begin to combine in groups the validity of these statements ceases. Fluorescence entirely ceases in such a group and absorption extends over wave lengths which a separate molecule is not able to absorb.

Walter's idea of the separate molecule seems to correspond closely with what is now known as the ion.

In 1894 E. Buckingham[2] performed a series of careful experiments to discover whether or not fluorescent substances are in a state of ionization. His investigations led to the conclusion that, at least in some cases, fluorescence is due to ionization and produced only by that part of a solution which is ionized. Certain ions, along with their other well known optical properties, possess this property of fluorescence.

The spectro-photometric work of Nichols and Merritt deals with many of the phenomena of fluorescent substances, only a few of which need be mentioned here. The following facts observed by them[3] for fluorescein are also true for resorufin as will be shown in the third part of this paper:

[1] B. Walter, Wied. Ann., 36, p. 518, 1889.
[2] E. Buckingham, Zeitschrift fur Physikalische Chemie, 14, p. 129, 1894.
[3] Nichols & Merritt, PHYSICAL REVIEW, Vol. 18, No. 6, 1904.

1. The characteristic fluorescence band is situated near the edge of the absorption band and is steeper on the side toward the violet.

2. As fluorescent light passes through greater thicknesses of liquid, the position of the maximum in the fluorescence spectrum is shifted toward the red.

3. The effect of diluting a fluorescent solution is similar to that of diminishing the distance through which the fluorescent light travels.

Method of Observation.

The instrument used for this work was the spectro-photometer of Lummer and Brodhun. The position of the collimator tubes *A* and *B* (Fig. 1), was adjusted until the image of the sodium line from the slit *c* coincided with the same line from slit *D* This line was set to division 10 of the vernier attached to the telescope, *T*, and the instrument clamped in this position.

The source of light was an acetylene flame *S* from which light was diffusely reflected by a block of magnesium carbonate, *n*, mounted at an angle of 45° with axis of the collimator *A*. For observations on transmission a similar block of magnesium carbonate was placed in front of the slit *D*.

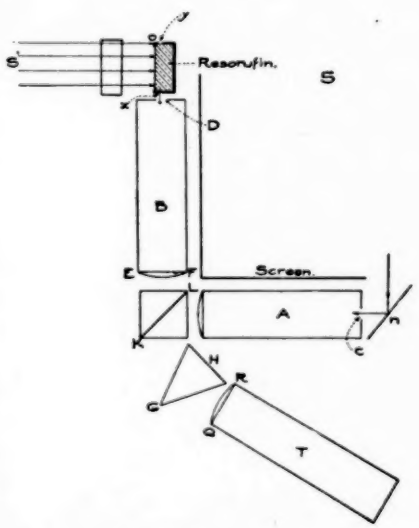


Fig. 1. Shows the apparatus arranged for measurements of fluorescence.

The work was performed in a room with black walls, the acetylene flame being the only source of light. Screens were adjusted so that no stray light could strike any part of the instrument and thus produce error.

The solution under consideration was placed in front of slit *D*, the width of which was kept constant during a single set of observations. The ocular lenses of the telescope were removed, the eye

being focused upon the face of the prism magnified by the objective of the telescope *T*.

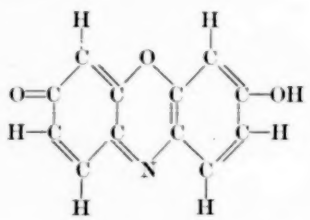
In making observations the width of slit *c* was adjusted by means of a micrometer screw until the central band of light reflected from *KL* was brought into the best possible coincidence with that transmitted through the upper and lower parts of the cube from *D*.

The results given represent an average of from 5 to 10 settings, the zero point of the screw attached to *c* being carefully determined and caution being taken to avoid error due to lost motion.

The hydrogen lines of a vacuum tube, together with a few of the Frauenhofer lines, were used for calibration.

COMPOSITION OF RESORUFIN.

Weselski's diazo-resorufin,[1] the fluorescent substance used in this investigation, has the formula



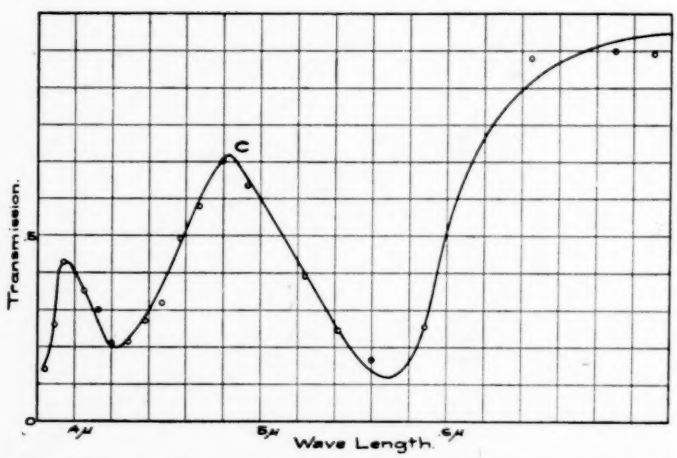


Fig. 2. Transmission spectrum of layer 1.075 cm. thick. Concentration 1/8.

[1] Berichte, 22, 3036. Acknowledgment should be made to Professor W. R. Orndorff for his kindness in preparing the resorufin used in this work.

Dissolved in absolute alcohol it is bright red in color with a sharply defined fluorescence band extending from .54 μ to the limits of the visible spectrum in the red. The transmission spectrum given in Table I. and Fig. 1 shows the absorption band corresponding to this, and also a smaller absorption band in the region of the extreme violet.

TABLE I.

Transmission through layer of resorufin 1.075 *cm. thick.*
Concentration 1/8.
I_0 = *Intensity of light before transmission.*
I = *Intensity of light after transmission.*
λ = *Wave-length.*

λ	I_0	I	$\frac{I}{I_0}$ = Transmission.
.384 μ	45	6	.111
.39	46	12	.261
.394	46	20.25	.438
.407	46	16	.347
.413	46	13.625	.297
.42	46	9.75	.213
.429	46	9.95	.217
.438	45.5	12.1	.266
.448	45.5	14.15	.32
.457	45.05	22.275	.497
.468	45.05	25.975	.579
.48	45.725	32.05	.70
.492	45.725	28.875	.63
.508	44.7	24.4	.538
.524	44.7	17.575	.394
.542	46.27	11	.241
.562	46.41	7.525	.162
.589	46.25	11.64	.253
.614	46.55	32.275	.706
.646	46.623	45.625	.981
.69	44.525	44	.99
.72	41.25	41	.99

For this work different concentrations of resorufin were used. These are merely relative and are indicated as "concentration $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, $\frac{1}{64}$ and $\frac{1}{128}$," the original solution being taken as $\frac{1}{1}$. All curves corresponding to the above concentrations are indicated by the letters *A*, *B*, *C*, *D*, *E*, *F* and *G* respectively.

ABSORPTION AND THICKNESS.

The first problem under consideration was, as stated above, to find whether a fluorescent solution acts like an optically perfect substance in obeying Lambert's law of absorption, *i. e.*, whether

$$I = I_0 e^{-\beta x}$$

where I_0 and I are the intensities before and after transmission, and x is the thickness of the absorbing layer.

To test this law the coefficient of absorption, β, was calculated from observations taken with cells of different inside thickness, the measurements of these cells being made with great care.

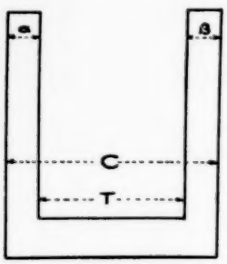


Fig. 3.

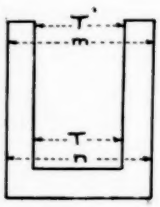


Fig. 4.

The larger cell was measured with micrometer calipers. Thickness of glass $= \alpha$, β (Fig. 3). Outside thickness of that part of the cell used for transmission $= C$. Inside thickness $= T$.

$$T = C - (\alpha + \beta) = 2.05 \text{ cm.}$$

In the case of small cell (Fig. 4), calipers could not be used to measure the thickness of glass. The cell was placed under a travelling microscope to measure the average inside thickness of the top. The outside thickness at the points indicated in the figure was measured with calipers.

$$T = T' + (n - m) = 1.075 \text{ cm.}$$

It was assumed that thickness of glass from top to bottom of cell remained constant since broken pieces of the same glass varied not more than .01 mm.

To determine the transmission, the cell containing the resorufin was placed in front of slit D (Fig. 1), care being taken that no

direct light from S should strike the cell, and light from the block of magnesium carbonate, in front of slit D (not shown in the figure), was transmitted through it. The reading of C was taken to get the relative intensity, I, of the light transmitted for different wave lengths. After each observation the cell containing resorufin was removed and an identical one filled with absolute alcohol put in its place. The reading of C in this case gave the value of incident light before absorption, I_0. From these observed values of I_0 and I, together with the thickness of the absorbing layer, the coefficient of absorption was computed.

As a check upon these results a different method of observation was used. Keeping D (Fig. 1) constant, the reading C_1 was taken for the light alone. A reading of C_2 was then taken with alcohol in front of C and resorufin in front of D.

$$\frac{C_1}{D} = \text{Incident light } (I_0),$$

$$\frac{C_2}{D} = \text{Transmitted light } (I),$$

$$\frac{\frac{C_1}{D}}{\frac{C_2}{D}} = \frac{C_1}{C_2} = \frac{I}{I_0}.$$

As a further check the positions of alcohol and resorufin were reversed, the alcohol being placed in front of D and the resorufin in front of C. Then

$$\frac{D}{C_1} = I, \qquad \frac{D}{C_2} = I_0,$$

$$\frac{I}{I_0} = \frac{C_2}{C_1}.$$

From these data the value of the coefficient of absorption for each wave length was found to be practically the same as that found by the first method and independent of the thickness of the cell. Absorption curves plotted from average values obtained by both methods, using cells of two thicknesses are identical, as shown in Fig. 5.[1] The

[1] Figures 5, 6, and 7 give only relative values of coefficients since they are drawn from data computed upon the basis of ordinary instead of natural logarithms. To get from the curves the absolute value of coefficients given in the tables multiply by 2.3.

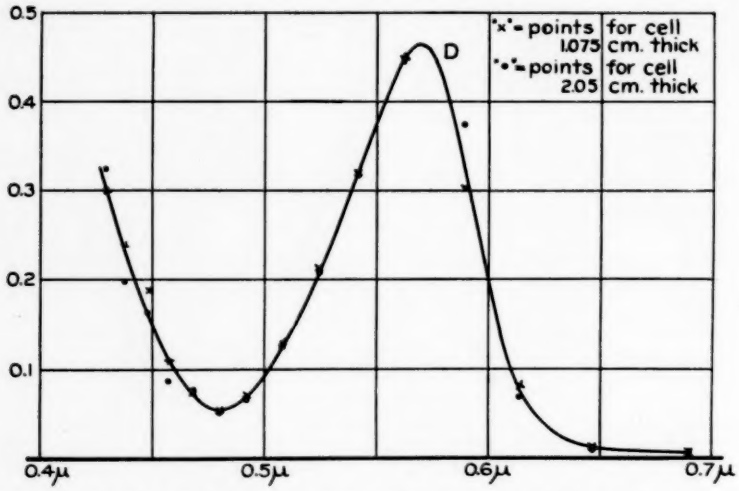


Fig. 5. Coefficient of absorption as computed from cells of different thickness.

absorption coefficients for different concentrations and also the data from which the computation was made are given in Table II.

TABLE II.

Coefficient of absorption computed from cells of different thickness.
Concentration = 1/16.
I_0 = *Intensity of light before transmission.*
I = *Intensity of light after transmission.*
β = *Coefficient of absorption.*

λ	Thickness of Cell = 1.075 cm.			Thickness of Cell = 2.05 cm.		
	I_0	I	β	I_0	I	β
.429 μ	79.9	35.76	.7476	81.85	19.95	.6884
.438	78.82	48.36	.4539	80.	25.93	.5495
.448	80.2	53.58	.3746	82.45	33.7	.4363
.457	79.49	62.55	.2223	80.6	48.3	.2495
.468	81.58	66.12	.1805[1]	80.36	54.5	.1702[1]
.48	78.94	70.01	.1175[1]	82.28	61.35	.1267[1]
.492	76.14	64.78	.15	80.5	57.05	.1678
.508	76.55	57.55	.2653	79.68	43.13	.2993
.524	76.8	45.83	.4808	78.93	29.58	.4786
.542	75.64	34.56	.7283	78.48	17.32	.7369
.562	75.91	25.37	1.02[1]	78.68	10.	1.0304[1]
.589	75.84	30.92	.8354	79.37	18.97	.6979
.614	75.19	63.41	.1579	79.85	54.08	.1899
.646	73.57	72.21	.0169	80.89	75.8	.0316
.69	64.93	63.85	.0148	71.33	69.2	.0144

[1] These values are average results from a number of observations.

It appears therefore that the absorption of resorufin is in accordance with Lambert's Law. Deviations from this law, if present, are at least too small to be detected by the experimental methods used.

Absorption and Concentration.

The second set of experiments was undertaken to study the relation between absorption and concentration and thus test the validity of Beer's law for a fluorescent substance, *i. e.*, "Increasing the concentration of a solution is equivalent to a like increase in thickness."

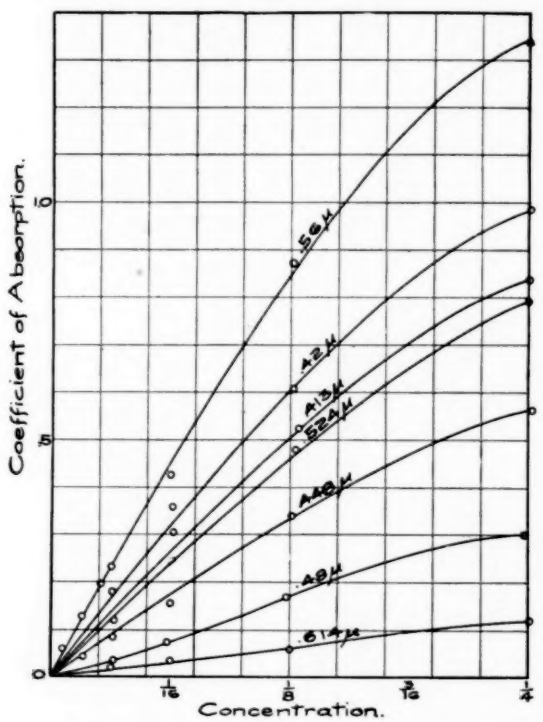


Fig. 6. Curves showing effect of change in concentration upon coefficient of absorption[1] of wave-lengths marked on curves.

The same method of observation was employed for this as for the preceding work, no changes in the apparatus being necessary. The coefficient of absorption was found for different concentrations, the solution being placed in a cell 2.05 cm. thick if dilute, and in cell 1.075 cm. thick if concentrated. This change of cell is permissible

[1] See footnote on page 363.

since, according to the results obtained above, Lambert's law of absorption applies to resorufin. The absorption coefficient of different wave lengths was thus obtained for seven concentrations.

Figs. 6 and 7 give the results of these observations. It will be noticed from these curves that the coefficient of absorption,

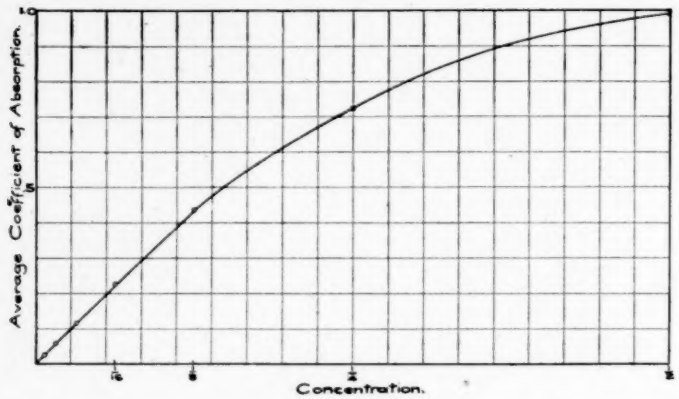


Fig. 7. Average coefficients of absorption[1] for different concentrations taken from Table III.

in the case of dilute solutions, increases in direct proportion to concentration. For concentrated solutions, this proportion fails, the concentration increasing more rapidly than the absorption. This is true for all the wave lengths; in every case the curve starts out as a straight line for dilute solutions and bends downward as higher concentrations are reached.

TABLE III.

Coefficient of absorption for corresponding wave-lengths in different concentrations.

λ	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
.413 μ	2.254	1.8814	1.2132	.7125	.3107	.1444	.0276
.42	2.806	2.2793	1.4237	.8533	.4360	.1984	.0775
.448	2.53	1.5364	.7935	.3565	.1860	.0897	.0368
.48	1.336	.6934	.3864	.1734	.0749	.0586	.0367
.524	3.162	1.8584	1.1247	.5349	.2783	.1453	.0692
.562	3.473	3.0797	2.0171	.989	.5441	.3036	.1442
.614	.3864	.3082	.1550	.0995	.0484	.0524	.0265
Average	2.2782	1.6624	1.0162+	.5313	.2683	.1417	.0597

[1] See footnote on page 363.

Fig. 7 shows the average coefficient of absorption for the seven wave-lengths as a function of the concentration. This curve is used later for finding the coefficient of absorption for different dilutions, especially careful measurements for the concentration 1/16, being taken as a basis of calculation. The values thus obtained, given in Table IV, were used in all subsequent computations involving the coefficient of absorption.

TABLE IV.

Coefficients of absorption computed from average of careful observations for concentration 1/16 *and average absorption concentration curve.* (*Fig.* 7.)

λ	1/2	1/4	1/8	1/16	1/32	1/64	1/128
.524 μ	2.1986	1.60471	.9841	.51313	.2599	.12995	.0651
.542	3.266	2.385	1.455	.76245	.38398	.19251	.09637
.562	4.3608	3.175	1.946	1.0177	.5154	.25783	.1288
.589	2.7324	1.995	1.219	.63733	.3227	.16146	.0807
.614	.49335	.36087	.22157	.115322	.05842	.0292	.0146
.646	.95588	.0698	.0428	.0223	.0113	.00575	.00283

The above results agree, in every respect, with those given by Walter.[1] Beer's law is true for dilute solutions but fails for greater concentrations, as is indicated by the deviation of the curve from a straight line. The straight form of the curve (Fig. 7) up to concentration 1/8 corresponds to what Walter calls "complete solution" in which, he says, the molecules are in a "separate state." Concentration 1/8 may be regarded as his "critical dilution" where a change seems to take place in the condition of the fluorescent substance. Solutions more concentrated than 1/8 correspond to those called by Walter "incomplete" in which "molecular groups" exist.

Interpreted according to the ionization theory the curve (Fig. 7) indicates that in dilutions less than 1/8 a state of complete or nearly complete ionization has been reached. At this point a change takes place, more resorufin being contained in the solution than is ionized. As the concentration increases, more and more of the solution remains undissociated. It appears that the undissociated resorufin is not only incapable of fluorescence, but is also much less effective in causing absorption than is the dissociated substance.

[1] B. Walter, Wied. Ann., 36, pp. 502 and 518, 1889.

FLUORESCENCE AND CONCENTRATION.

For observation of the fluorescence spectrum the spectro-photometer was adjusted as before. In front of slit D (Fig. 1) was placed a glass cell 5.4 cm. long containing the resorufin solution. This cell was entirely covered with black paper except for a space about 1.5 cm. high across the bottom of the face next to the exciting light S', and two narrow strips x and y. The opening x was to allow light to enter collimator slit, while y, directly opposite, was used only for adjusting. The source of illumination used to produce fluorescence was a bank of four acetylene flames S'. Between these and the fluorescent solution was placed a glass cell filled with water to prevent the heating of the resorufin. The comparison source was another acetylene burner, S, light from which was reflected into the slit C, by a block of magnesium carbonate, n. The cell containing the resorufin was so placed that light from the whole layer of solution next the inside surface of glass came through the slit D of the collimator.

It is clear that a portion of the fluorescent light is absorbed by the solution before reaching D; and attention has already been called to the fact that this absorption will be different for different parts of the fluorescence spectrum. If the fluorescence is measured

Fig. 8.

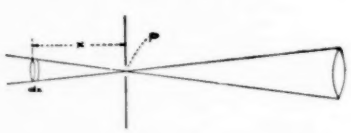


Fig. 9.

in the manner indicated above it is therefore necessary to apply a correction for absorption before the typical fluorescence spectrum can be determined. Two methods of making this correction have been used. In the first method the necessary correction was computed as follows:

Let P be any point in the slit (Fig. 8). The source of the light reaching P is a cone in the fluorescent liquid converging toward P. The angle of this cone is determined by the aperture of the object glass, EF, of the collimator. Any part of this cone cut off by the

glass walls of the cell or by the upper surface of the solution is supplied by total reflection.

Consider a disk bounded by two circular sections of this cone at distances x and $x + dx$ respectively from the apex, P (Fig. 9). The amount of fluorescent light reaching P from such a disk as this will be independent of x, provided no absorption takes place, for, while the area of the section varies as x^2, the intensity of the light reaching P from each small portion of the disk varies as $1/x^2$. The fluorescent light that would reach P from such a disk if there were no absorption is therefore kdx, where k is a function of the wave-length, λ.

Since the light emitted by each section of the cone is in part absorbed, we have for the light reaching P from one of the disks

$$di = kdx \cdot e^{-\beta x}$$

and the total light reaching P from the whole cone is

$$i = k \int_0^a e^{-\beta x} dx$$

where a is the thickness of the fluorescent solution. Hence

$$i = k \cdot \frac{1 - e^{-\beta a}}{\beta}$$

and

$$k = \frac{\beta i}{1 - e^{-\beta a}}.$$

While the i in this expression represents the light reaching one infinitesimal portion of the slit, it is clear that the total light reaching the slit is proportional to i. It is also evident that k is proportional to the total amount of light, f, of the wave-length considered that is emitted by the fluorescent substance per unit volume. Hence

$$f = \frac{k\beta I}{1 - e^{-\beta a}}.$$

The curve showing the relation between f and λ is the "typical fluorescence spectrum."

TABLE V.

Observed fluorescence intensity before correction is made for absorption. Measurements made according to Method I, fluorescence excitation extending over whole face of cell.

λ	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
.524 μ	1.77	2	2.1	2	2.08	2.4
.542	1.86	2.1	2.2	2	2.13	2.41
.562	3.46	4.67	5.61	7.66	7.43	7.266
.589	30.29	46.44	56.64	34.87	23.21	16.17
.614	79.46	95.49	95.27	34.03	17.63	11.62
.646	86.6	76.3	66.27	17.73	8.9	6.88
.69	59.27	42.42	46.23	12.67	7.28	

TABLE VI.

Observed fluorescence intensity reduced to such a scale as to make intensity of wave-length .589 μ. The same as observed fluorescence in Table VIII.

λ	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
.524 μ	5.38	4.08	3.192	3.32	3.578	3.116
.542	5.65	4.284	3.344	3.32	3.66	3.229
.562	10.52	9.53	8.53	12.715	12.78	9.736
.589	92.17	94.64	86.06	57.95	40.41	21.68
.614	241.558	194.8	144.81	56.49	30.32	15.57
.646	263.26	155.65	100.73	29.43	15.308	9.22
.69	180.18	86.54	70.27	21.03	12.52	

To investigate the effect of concentration upon the position of the fluorescence band observations were made in six concentrations. Table V. gives values of observed fluorescence before any correction is made for absorption. Table VI., graphically represented in

TABLE VII.

Corrected fluorescence. Value of f calculated from Table V. according to formula $f = I\beta/(1 - e^{-\beta a})$.

λ	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
.524 μ	2.841	1.968	1.148	.67	.53	.52
.542	4.436	3.056	1.74	.86	.632	.566
.562	10.98	9.088	5.734	4.196	2.558	1.85
.589	60.438	56.61	37.2	13.62	6.35	3.665
.614	33.34	29.757	23.55	7.27	3.455	2.203
.646	19.31	15.55	12.83	3.339	1.65	1.217

TABLE VIII.

Intensity of fluorescence of different concentrations at wave-length .589 μ.

	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
Observed fluorescence.	75.5	92.17	94.64	86.06	57.95	40.01	21.68
Corrected fluorescence, *i. e.*, value of *k* as obtained from formula.	206.115	183.879	115.366	54.85	22.53	11.044	4.86

Fig. 10, gives the same sets of observations so reduced in scale as to be comparable in intensity with each other. Thus reduction was made by multiplying the data for each concentration by such a factor as to give wave-length .589 μ the same value as that given as the observed fluorescence of the corresponding concentration in Table VIII.

The curves in Fig. 10 show the observed values of I as a function of λ for six different concentrations of the solution. The shift in the maximum caused by a change in concentration is here well marked.

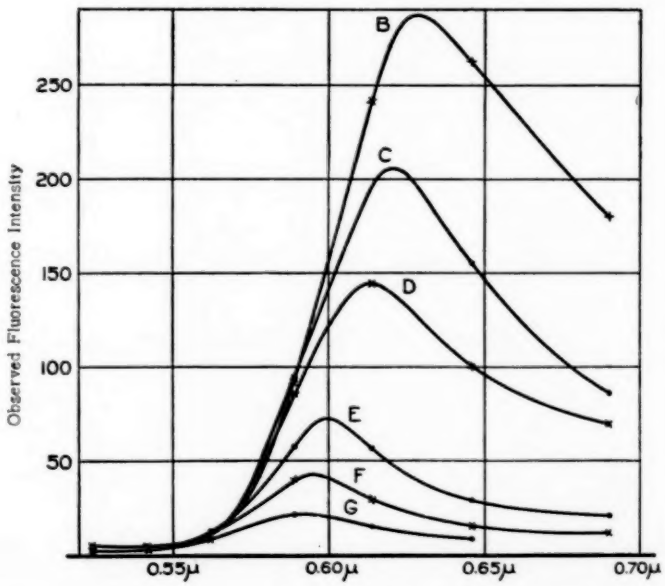


Fig. 10. Observed fluorescence intensity, showing shift of maximum, with change in concentration.

Table VII. gives the result of correcting values in Table V. for absorption according to the above formula, the value of f, which

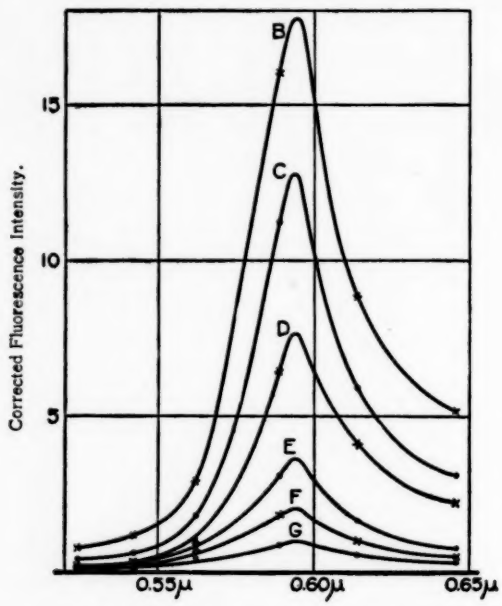


Fig. 11. Fluorescence curves corrected for absorption.

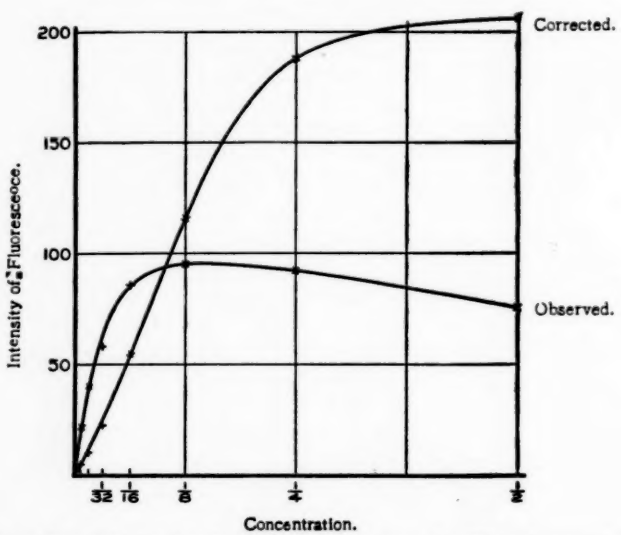


Fig. 12. Intensity of observed and corrected fluorescence for different concentrations at wave-length .589 μ.

is proportional to actual fluorescence intensity (see page 369), being found in each case. These values are plotted in Fig. 11 according to an arbitrary vertical scale which makes the height of each curve approximately proportional to intensity of fluorescence for the corresponding concentration. It will be observed that these curves are similar in form, the maximum wave-length being approximately the same, about .595 μ.

For purposes of comparison a series of measurements was made to determine the relative intensity of different concentrations at wave-length .589 μ, keeping all conditions constant. Table VIII. shows the results. In Fig. 12 the curves marked "observed"

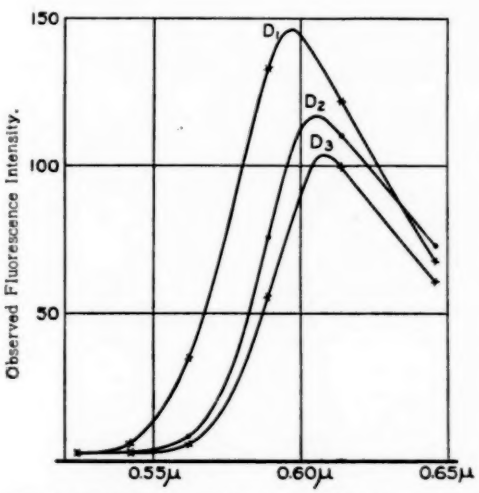


Fig. 13. Observed fluorescence produced by light from 1 mm. section passing through different thicknesses of solution.

Thickness of $D_1 = 1$ mm.
Thickness of $D_2 = 1$ cm.
Thickness of $D_3 = 2$ cm.

gives the actual observed fluorescence. The "corrected" curve has for ordinates the value of f computed from the formula (page 369) and shows the relative intensity of actual fluorescence in different concentrations.

The following method of obtaining the corrected fluorescence curves was used as a check upon the first, the final results being obtained yb a graphical, rather than mathematical procedure.

The apparatus was set up as before except that the light exciting fluorescence, instead of striking the whole face of the glass, was allowed to strike only a vertical section 1 mm. in width. The side of the cell next to the exciting light S' was covered with a black paper screen having a vertical opening 1 mm. wide, through which light was admitted. This opening was set at different distances from the end of the cell and the fluorescence intensity was measured for three or four different positions. In order to make possible accurate measurements of the distance from the edge of the glass, a

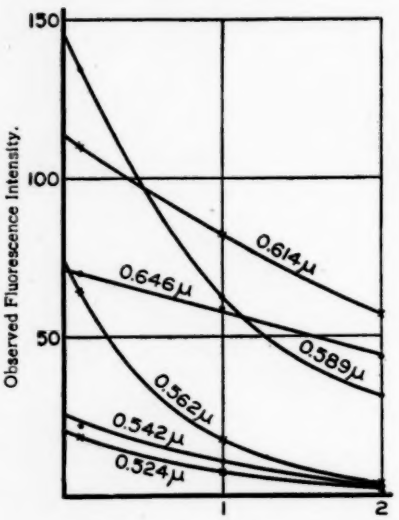


Fig. 14. Variation in intensity of observed fluorescence from 1 mm. section transmitted through different thicknesses of solution.

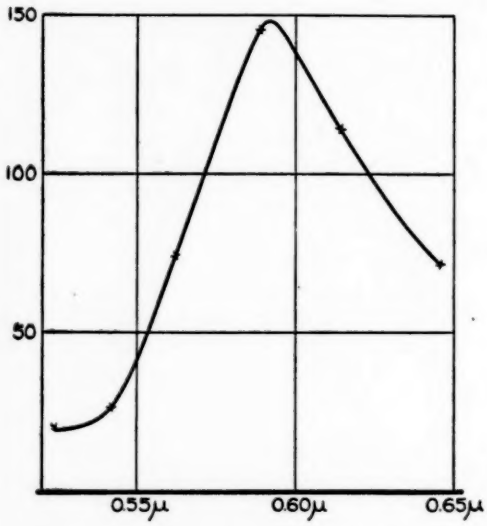


Fig. 15. Fluorescence corrected for absorption by graphical method. Concentration = 1/8.

scale was etched upon the face of the cell just above the level of the collimator slit.

The effect of absorption upon the position of the maximum of the fluorescence spectrum is well shown in Fig. 13, in which the three curves were taken with the opening at different distances from the face of the cell.

In order to correct for absorption, curves similar to those shown in Figs. 14 and 15 were plotted for each solution. These curves

show the variation in the intensity of the fluorescent light with the thickness of the liquid through which the light passes. From the intercept of one of these curves upon the y axis the intensity of fluorescence can be found when the thickness becomes zero. In such a case there is no absorption. The error of extrapolation was reduced to a minimum by taking one point very close to the edge of the glass.

The corrected values of fluorescence intensity thus obtained were used in plotting the accompanying fluorescence curve in Fig. 15. The same procedure was followed in the case of each solution.

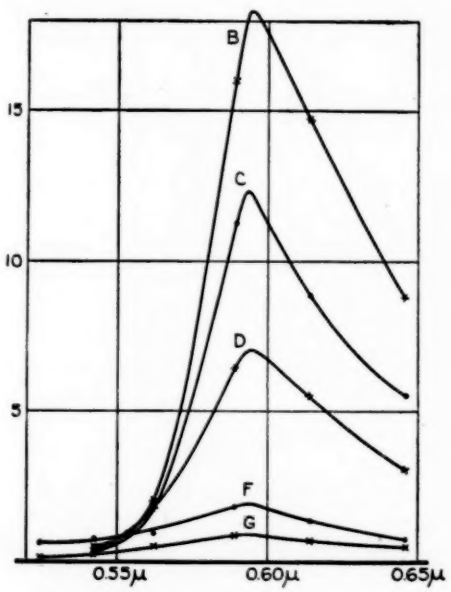


Fig. 16. Fluorescence curves corrected for absorption by graphical method. Vertical scale same as for Fig. 11.

The observations and results obtained by this graphical method are given in Table IX. The corrected fluorescence spectra obtained in this way are plotted together in Fig. 16, the vertical scale being such that values for wave-length .589 μ are the same as the values for the corresponding concentration in Fig. 11.

TABLE IX.

Observed fluorescence of section 1 *mm. wide from which light is transmitted through different thicknesses of solution. The column marked* 0 *thickness gives fluorescence intensity corrected for absorption by graphical method, i. e., by extrapolation from curves similar to those in Fig. 14.*

Concentration 1/2.

λ	1.5 mm.	5 mm.	1 cm.	0
.524 μ	1.75		1.1	1.5
.542	2.525	1.6	1.2	2
.562	14.3	3	1.95	12.5
.589	66.24	41.5	29.63	114
.614	94.49	70.73	61.16	103
.646	42.4	42	42.5	43

Concentration 1/4.

λ	1.5 mm.	5 mm.	1 cm.	0
.542 μ	2.83	2.1	1.3	3
.562	9.075	4.1	2.325	13.8
.589	71.375	45.88	21.38	103.5
.614	88.07	73.73	64.66	95
.646	51.46	48.7	54.375	52.3

Concentration 1/8.

λ	1.5 mm.	5 mm.	1 cm.	0
.524 μ	2.65	2.1	1.73	2.5
.542	3.9	2.6	2.66	4
.562	34.15	12.083	7.525	50
.589	95.67	69.678	49.56	109
.6	101.75	79.5	63.33	117
.614	79.725	68.4	56.5	90
.646	34.68	33.6	31	36

Concentration 1/16.

λ	1 mm.	1 cm.	2 cm.	0
.524 μ		2.83	3	3.5
.542	5.92	2.97	2.83	8
.562	34.87	8.62	5.56	42
.589	132.7	75.95	55.43	144
.614	121.42	110.3	99.6	124.5
.646	67.36	72.7	60.27	70

Concentration 1/64.

λ	1.5 mm.	5 mm.	1 cm.	0
.508 μ	3.47	3.81	3	4
.524	4.83	3.75	3.75	4
.542	6.16	4.9	4.23	7
.562	61.77	38.5	25.55	76
.589	145.85	138	125.05	150
.614	110.45	104.86	96.15	113.5
.646	58.1	50.25	31.7	60

Concentration 1/128.

λ	1.5 mm.	5 mm.	1 cm.	0
.524 μ	4.17	4.47	3.45	4.5
.542	6.53	6.1	5.33	6.8
.562	25.2	23.66	17	26
.589	49.17	49.5	47.38	49.5
.614	39.66	37.66	38.33	39.5
.646	27.83	25	27.5	28

A comparison of the curves of Figs. 11 and 16 shows that the results obtained by the two methods are the same. The typical fluorescence curves are all similar in form and the position of maximum fluorescence (about .595 μ) remains constant for all dilutions. The shift in the observed fluorescence maximum is therefore due entirely to absorption.

This fixed position of maximum fluorescence seems to be consistent with the theory of ionization. According to Buckingham, ions may have some of the same optical properties as other substances and fluorescence is one of these properties. If only the ions fluoresce the position of maximum fluorescence would evidently remain constant whether the material of the solution were all ionized or not.

This fixed position of maximum fluorescence is also consistent with the theory of Nichols and Merritt[1] that fluorescence is caused by an unusual kind of dissociation similar to that produced in a gas by the action of Röntgen rays. That part of the solution which, during the process of change, produces fluorescence does not give evidence of any effect due to material not dissociated beyond that of absorption.

[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 19, No. 1, 1904; Vol. 22, No. 5, 1906.

SUMMARY.

The results of the above investigation upon resorufin, as a typical fluorescent substance, taken in connection with the work of B. Walter and Nichols and Merritt, seem to establish the truth of the following statements:

1. Fluorescent solutions are optically perfect substances, *i. e.*, they obey Lambert's Law.

2. Beer's law, *i. e.*, that increase of concentration is equivalent to increase in thickness, is true for dilute but not for concentrated solutions.

3. A change in the concentration of a fluorescent solution has no effect upon the typical fluorescence spectrum.

PHYSICAL LABORATORY
OF CORNELL UNIVERSITY.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-SIXTH MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, March 2, 1907.

In the absence of the president and vice-president Mr. W. C. Sabine was nominated as chairman.

Professor O. Lummer, of the University of Breslau addressed the Society on The Temperature of the Sun and recent Solar Theories.

The following papers were then presented:

1. On the Forces on the Interior of a Conductor Carrying Current. E. F. NORTHRUP.

2. The Radiation from, and the Melting Points of, Palladium and Platinum. C. W. WAIDNER and G. K. BURGESS.

3. The Viscosity of Certain Isomeric Ether Compounds. F. M. PEDERSON.

4. The Effect of Frequency upon the Capacity of Absolute Condensers. J. G. COFFIN.

5. The Physical Nature of Meteor Trains. C. C. TROWBRIDGE.

6. On Atmospheric Drifts above fifty Miles from the Surface of the Earth. C. C. TROWBRIDGE.

7. The Equations of the Fog Chamber. (By title.) CARL BARUS.

8. The Current carried by Canal Rays in a Discharge Tube. C. C. PERRY.

9. Note on the Hissing Metallic Arc. W. G. CADY.

10. The Relation between Luminosity and Electrical Conductivity. F. L. TUFTS. Adjourned.

ERNEST MERRITT,
Secretary.

NOTE ON THE FLUORESCENCE OF SODIUM VAPOR.[1]

BY ERNEST MERRITT.

THE recent experiments of R. W. Wood have shown that the fluorescence spectrum of sodium vapor, which exhibits great complexity when excited by white light, is relatively simple when suitable mono-

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 1, 1906.

chromatic exciting sources are used. The complex spectrum produced by white light appears to result from the superposition of a number of groups of lines, the lines of each group forming a spectral series. Excitation by light corresponding to one line of a group produces a fluorescence spectrum which contains only lines of the same group; but the distribution of intensities among the lines of a group appears to depend upon which line is directly stimulated by the exciting light.

Although none of the numerous attempts to devise a mechanical model of an atom have proven successful, it can scarcely be doubted that the lines of a given group or series correspond to the different natural periods of vibration of one connected system. But while it is natural to expect that the line corresponding to one mode of vibration of such a system will be stimulated by exciting light of the same frequency, it is at first difficult to see how such monochromatic excitation can also set up vibrations of different periods. In general stimulation of a mechanical system by resonance is effective only in the case of exact or nearly exact unison; even a harmonic overtone cannot be stimulated by its fundamental, or by another tone of the same series.

It has occurred to the writer that this difficulty may be met by taking into consideration the effect of collisions between atoms. Between collisions a considerable amount of energy will be absorbed in the form of vibrations of the particular type that is in resonance with the exciting waves. Whatever may be the nature of what we call a collision, it seems certain that forces then come into action which will tend to disturb the

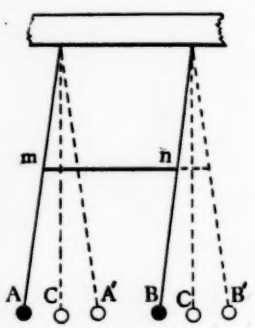


Fig. 1.

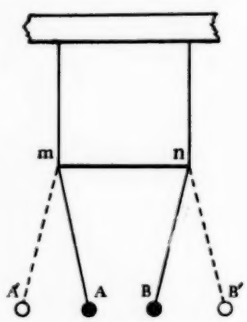


Fig. 2.

condition of vibration of the atoms. In general the energy stored between collisions will be partly changed into translational energy and partly transferred to other modes of vibration. The manner in which it is distributed among the various possible types of vibration may readily depend upon which type of vibration was originally exerted.

The following will serve as a simple mechanical illustration of the

principle involved. Imagine two simple pendulums, of equal mass and length, connected by a rigid massless rod *mn*. The two principal modes of vibration of such a system are shown in Figs. 1 and 2. In one case *A* and *B* vibrate in the same phase and with the same period as though *mn* were absent. In the second case the rod *mn* remains at rest and *A* and *B* vibrate in opposite phase, the period being that of a pendulum of length *mA*. Let the system be set into vibration in the manner shown in Fig. 1, and as the mass *A* passes through the vertical let it collide with a heavy elastic body, so as to have its motion reversed. After such a collision the system will vibrate in the type of vibration of Fig. 2, with a period shorter than before. In such a case the energy of one type of vibration is completely transformed into that of another type. In general the collision would be less complete and the subsequent motion would be complex, involving vibrations in both of the principal modes.

It might be urged against this explanation of the phenomena that the effect of collision is merely to add certain vibrations, which in the subsequent motion are superposed upon the original vibration: but the effect of collisions alone, without excitation by light, is insignificant, as is indicated by the small temperature radiation of the gas; hence no effect as great as required to explain Wood's results can be expected. This line of reasoning leads to the suggestion that the effect of collision between *vibrating* atoms may be quite different from the effect of ordinary collisions. In a vibrating atom the electrons will at times be far removed from their equilibrium positions and may in consequence be greatly disturbed by the field of a neighboring atom.

The Hissing Point of the Metallic Arc.[1]

By W. G. Cady.

THIS paper is a preliminary report dealing chiefly with the arc between iron and copper terminals. Mr. H. D. Arnold, Assistant in Physics, is associated with the writer in this work, which is being carried on with aid from the Elizabeth Thompson Science Fund.

The fact should not be overlooked that the so-called iron arc is, in air, an arc between molten globules of magnetic oxid of iron. By letting the arc burn until it has become normal, observations can be made that compare in accuracy with those in the case of the carbon arc.

Observations were first made to verify the generally accepted linear equation $E = a + bl$ connecting volts across arc with length of arc for iron electrodes. When curves were drawn showing the potential drop as function of the length for different currents, it was found that the curves

[1] Abstract of a paper presented at the New York meeting of the Physical Society, December 29, 1906.

had approximately a parabolic form, suggesting that the equation should have a term involving $\sqrt{l}$.

The difficulty encountered in obtaining reliable observations in the neighborhood of one ampere led Mr. Arnold to the detection of an abrupt change in the iron arc, analogous to the hissing point of the carbon arc. For currents below one ampere, the arc burns quietly and there is no well-defined spot of light on the globule at the anode. As the external resistance is decreased so that the current increases beyond a value depending largely on the curvature of the globule, the arc suddenly contracts, a bright spot appears on the anode, hissing commences, potential difference drops and current increases slightly. Experiment showed that the effect is confined mainly to the anode. When the current is decreased, the change back to the quiet stage does not take place until the current has become smaller than it was when hissing commenced, due doubtless to the high temperature at the anode. From the point of view of spectroscopy, it would be of considerable interest to find out whether the spectrum of the iron arc suffers a change at the hissing point. A brief examination showed nothing further than a general brightening of lines, but the question whether all lines are brightened to the same degree deserves attention.

When the current is increased to about two amperes, the iron arc emits a whistling sound, and the spot at the anode has a tendency to travel around rapidly, describing a circular ring. This recalls Trotter's observation of the rotation of the hissing carbon arc. It is planned to examine this phenomenon more closely, with the aid of an oscillograph.

With copper electrodes the hissing point can also be found. It occurs, with electrodes 6 mm. thick, when the current is about 0.5 amp., with about 110 volts across the arc. The arc between aluminium electrodes was too unsteady for the detection of the effect. Zinc has thus far shown no hissing point. Something resembling a hissing point was found with an arc in air between a mercury anode and carbon cathode, but this may have been due to disturbing causes.

Lecher's assertion that the iron arc is a discontinuous discharge, while the copper arc is perfectly continuous, was put to the test for both the quiet and the hissing stages. A bolometer was substituted for the hot wire used by Lecher, but it soon became evident that the capacity and self-induction of the bolometer circuit tended to set up oscillations, causing a "singing" iron arc. This fact tends to discount Lecher's conclusions and to make the method inapplicable. Good results were obtained by connecting a self-inductance of low resistance in series with the arc. The bolometer and condenser in series were then connected in parallel to the self-inductance. In this way the bolometer became heated by oscillatory currents set up in the arc, without danger that the bolom-

eter circuit could disturb the conditions in the arc. The results are briefly these: the carbon and iron arcs, when quiet, are continuous; when hissing, they are oscillatory. The copper arc seems always to be oscillatory, and the smaller the current, the more is the bolometer heated. This point, as well as bolometric tests with other metals, is soon to be investigated.

The Equations of the Fog Chamber.[1]

By Carl Barus.

In my earlier papers, greater symmetry in the final results was obtained by the use of $p - \pi$ (where p is the total pressure and π the vapor pressure of the saturated gas) both in the isothermal and the adiabatic equations. But for the purposes of the fog chamber the correction thus made necessary is too large. Hence the following equations should be used.

Let p, π, ρ, τ, denote the total pressure, the vapor pressure, density and absolute temperature of the saturated gas, c and k the specific heats. When the variables are primed let them refer to the vacuum chamber, if unprimed to the fog chamber. Let subscripts distinguish the different thermodynamic states. Isothermally we have throughout $p - \pi = R\rho\tau$ in eight different cases; adiabatically $\tau/\tau_1 = (p/p_1)^{1-c/k}$ in two different cases.

Let the initial states of the fog chamber (before exhaustion, chambers separated) be given by p, ρ, τ, and of the vacuum chamber by p', ρ', τ; their final states when in communication after exhaustion by p_3, ρ_3, τ. Let their volume ratio be $[v/V]$.

If the two chambers had been separated immediately after exhaustion and before any condensation or heating ensued (subscript 1 referring to adiabatic conditions)

$$(p_1 - \pi_1)/p_1^{1-c/k} = \frac{(p_3 - \pi)(1 + [v/V])}{p'^{(1-c/k)}(1 + (\pi_1' - \pi_1)/(p - \pi_1)) + [v/V]p^{1-c/k}}$$

with a similar equation for the vacuum chamber. The volume expansion is given by

$$v_1/v = \frac{p}{p_3 - \pi} \frac{(p'/p)^{1-c/k}(1 - \pi_1'/p_1^{1-c/k}) + [v/V](1 - \pi_1/p_1^{1-c/k})}{1 + [v/V]}.$$

If each chamber is now allowed to reach atmospheric temperature (subscripts 2 denoting isothermal conditions)

$$p_2 - \pi = p^{1-c/k}(p_1 - \pi_1)/p_1^{1-c/k}$$

with a similar equation for the vacuum chamber.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, March 2, 1907.

If the temperature of the fog chamber is heated by the condensation of water alone from the adiabatic temperature τ_1 before condensation, to $\bar{\tau}_1$ after condensation, if d_1 is the density of water vapor at τ_1 and $\bar{d}_1$ at $\bar{\tau}_1$ we may write for the determination of $\bar{\tau}_1$

$$\bar{d}_1 = \left(d/(p-\pi) - \frac{\rho c}{L}\frac{\bar{\tau}_1 - \tau_1}{p-\pi} \right)(p_2 - \pi)$$

where c is the specific heat of air at constant volume and L the latent heat of evaporation. Hence the water precipitated per cubic centimeter is

$$m = \frac{\rho c}{L}\frac{p_1 - \pi_1}{p-\pi}\left(\frac{p}{p_1}\right)^{1-c/k}(\bar{\tau}_1 - \tau_1)$$

where p_1 may usually be replaced by p_2.

If the chambers are separated immediately after condensation takes place and before other appreciable heating occurs the p_1, ρ_1, τ_1, of the fog chamber will change to $\bar{p}_1$, $\bar{\rho}_1$, $\bar{\tau}_1$, solely from condensation, and this in turn to $\bar{p}_2$, $\bar{\rho}_2$, $\bar{\tau}_2$, when isothermal conditions are regained by heating from without. We then obtain for the fog chamber

$$\bar{p}_2 - \pi = (\bar{\rho}_1/\rho_1)(p_1 - \pi_1)(p/p_1)^{1-c/k}$$

where

$$\bar{\rho}_1/\rho = \frac{\tau_1}{\bar{\tau}_1}\frac{1 + [v/V](\tau_1'/\tau_1) + (\bar{\pi}_1' - \bar{\pi}_1 - (\pi_1' - \pi_1))/(p_1 - \pi_1)}{1 + [v/V](\tau_1'/\bar{\tau}_1)}$$

with similar expressions for the vacuum chamber. Since $\bar{\tau}_1$ and $\bar{\rho}_1$ are given, $\bar{p}_1$ may also be computed.

Finally we have in general

$$\begin{aligned}(p_2' - \pi) + [v/V](p_2 - \pi) &= p' - \pi + [v/V](p - \pi) \\ &= (1 + [v/V])(p_2 - \pi)\end{aligned}$$

or

$$[v/V] = (p_2 - p')/(p - p_2).$$

CARL BARUS.

BROWN UNIVERSITY,
PROVIDENCE, R. I.